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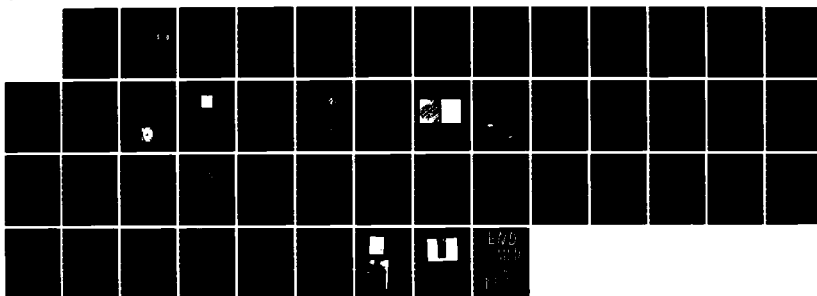
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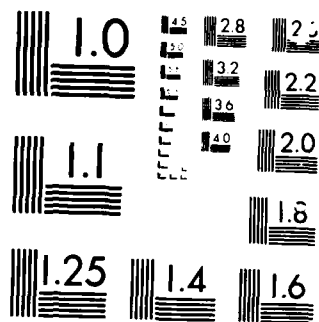
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MICROCOMPOSITE PROCESSING AND APPLICATIONS

Robert F. Kovar
Richard W. Lusignea

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350 Second Avenue
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March 1986

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Sol-gel reagents were successfully infiltrated into microfibrillar regions of water-swollen PBT films at loadings which exceeded 50 percent by weight. PBT/sol-gel glass microcomposite films containing rigid silica glass and silicone elastomer were prepared by reaction with tetramethoxysilane and dimethyldimethoxysilane, respectively. The amount of sol-gel glass introduced into PBT film was controlled by variation of sol-gel reagent concentration. Densification of PBT/sol-gel glass microcomposite films at moderate temperatures and pressures decreased film thickness and increased stiffness. Optical and scanning electron microscopy indicated that sol-gel reagents had uniformly infiltrated microfibrillar regions of PBT, forming interpenetrating networks. Pyrolysis of PBT/sol-gel glass samples in air produced continuous, wispy, translucent films of silica residue, providing evidence of previous sol-gel glass morphology within PBT film interiors.											
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Dense, well-consolidated laminates were prepared using PBT/sol-gel glass microcomposite films, and sol-gel reagents or adhesives as binder resins. These results provided methods for fabricating useful structures with improved stiffness, impact-resistance and interlaminar adhesion.

Phase I of this program demonstrated the feasibility of significantly improving PBT film properties by infiltration with sol-gel glass reagents. Phase II will address the following: ~~analysis of~~ PBT/sol-gel glass morphology, development of sol-gel reagent infiltration processes, lamination and coating of PBT films and fabrication of test samples, to demonstrate improved performance over other materials.

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1. PROJECT SUMMARY

Poly(benzobisthiazole) (PBT) is an ordered polymer characterized by a rigid, rod-like structure that exhibits extraordinary thermal and mechanical properties. The development of PBT into useful structural materials has been hindered by poor compressive properties and inadequate adhesion to a variety of adhesive resins.

Phase I of this study evaluated the feasibility of improving compressive strength and adhesive properties of PBT films by infiltration of sol-gel glass reagents into the microporous interiors of water-swollen films. We have successfully infiltrated a variety of sol-gel reagents into PBT films, significantly changing their properties. The extent of infiltration was readily controlled by adjusting reagent concentration and film immersion times. PBT films containing rigid glass and soft elastomer were prepared using selected sol-gel reagents. Certain sol-gel formulations were used to infiltrate, then bind multiple PBT films together into transparent, consolidated laminates.

The Phase I study demonstrated the feasibility of producing microcomposite materials by combining ordered polymers (as exemplified by PBT-polyphenylene benzobisthiazole) with sol-gel glass materials. The following specific objectives were met:

1. PBT/glass microcomposite films 0.005 in. thick were produced at practical temperatures, pressures and process times. Analysis showed that the ratio of PBT to glass could be varied by processing conditions, and that a very fine sub-micron network had been formed.
2. PBT/sol-gel glass microcomposite films were laminated by hot-pressing and by adhesively bonding the layers, showing the feasibility of practical fabrication techniques.
3. The ultimate compressive strength and stiffness of PBT/sol-gel glass films was significantly increased over pure PBT films. Ultimate flexural strengths of 96,000 psi were computed from three-point flexure tests, showing improved compressive strength of microcomposites compared with typical PBT film compressive strength. An acceptable degree of tensile strength was maintained - in proportion to the volume of PBT.

In addition to the specific objectives above, the Phase I program evaluated a range of six sol-gel glass formulations, developed two techniques for microcomposite processing, and measured important properties of the materials including dimensional stability, moisture absorption and thermogravimetric behavior.

The major tasks facing the Phase II program will be:

- Gaining a full enough understanding of the microcomposite material structure and behavior to direct and drive future development
- Scaling up of processing techniques developed in Phase I to provide quantities of material for test and evaluation

- Fabricating, testing and evaluating samples of the materials to meet applications requirements and compete in today's arena of high performance materials.

PBT/sol-gel microcomposites offer the promise of a new class of materials with high performance tailorable properties, small-scale homogeneity, and ease of fabrication. Rapid development and fulfillment of this promise will require predictable behavior, an engineering data base, and process condition "recipes" for producing controlled property materials. A behavioral model is needed for describing the mechanics of the microcomposites. This is likely to be based on mechanics of fiber-reinforced composites, but will also include effects such as "micro-buckling" observed in organic materials. The relationships between properties and processing will be needed to achieve repeatable performance. The dimensional stability, dielectric constant, toughness, fatigue resistance, and temperature capability correspond to particular precursor materials and process conditions which need to be determined.

PBT/sol-gel microcomposite materials meet applications such as solar array panels for spacecraft, high temperature aerospace structures, dimensionally stable electronic packaging, and low radar observable, hardened materials for SDI. The Phase II program will advance the materials and processing science for ordered polymer/sol-gel glass microcomposite materials. The proposed program will build upon Phase I results to determine structure-property relationships, analyze microcomposite physical behavior, identify applications and develop processing and fabrication techniques.

The Phase II program will provide test samples and small-scale prototypes for evaluation of high temperature properties, machinability, and specific mission performance for these applications.

The discussion in Section 2 will give the reader a background in PBT ordered polymers and sol-gel glass materials. Subsequent sections will discuss:

- Microcomposite processing methods developed in Phase I - Details of the solution processing techniques
- Film lamination and coating - Means to make engineering structures
- Material testing and evaluation - Flexural testing showing improved compressive properties.

Technical personnel associated with the Phase I effort were:

Mr. Richard W. Lusignea - Principal Investigator
 Dr. Robert F. Kovar - Senior Polymer Chemist
 Mr. Wesley J. Ishida - Staff Engineer

2. BACKGROUND

Understanding of the objectives of this program, the importance of the achievements of Phase I and the proposed activities for Phase II requires some familiarity with the unusual materials and novel processes involved. The following subsections introduce:

- PBT (poly p-phenylene benzobisthiazole film)
- IPNs (interpenetrating networks)
- Sol-gel processing.

2.1 PBT Film

PBT is a member of a new class of polymeric materials collectively referred to as ordered polymers. As a result of their rigid rod-like molecular structures, these materials form liquid crystalline solutions from which extremely strong, stiff fibers and films have been processed. The U.S. Air Force Materials Laboratory (AFML) has developed rod-like polymers with the best combination of strength, stiffness, thermal capability, and environmental resistance (1-3). Figure 1 illustrates the molecular structure of PBT. Tables 1 and 2 summarize some of the properties achieved to date with PBT fiber and film.

The fiber and film-forming processes involve several operations in which a polymer solution undergoes a succession of structural changes, leading to the final solid, as outlined in Table 3. In the coagulation stage a liquid to solid phase transition is induced, either by diffusion of a non-solvent or by a decrease in temperature. It is reasonable to assume that the structure formed by this phase transition is the basis for the structure of the final solid.

On the basis of electron-microscopic observation, Professors Farris and Thomas at the University of Massachusetts conclude that the structure formed during the coagulation stage of PBT fiber spinning is an interconnected network of highly oriented microfibrils of 80 to 100A diam. Figure 2 shows the structural model for wet coagulated fiber (4). Such fibers have been dried under tension in order to produce the high tensile properties noted above. However, instead of drying the coagulant from the network, it can be replaced by a variety of materials, forming a microcomposite, which has the strength of the PBT, but with other properties modified by the infiltrating materials.

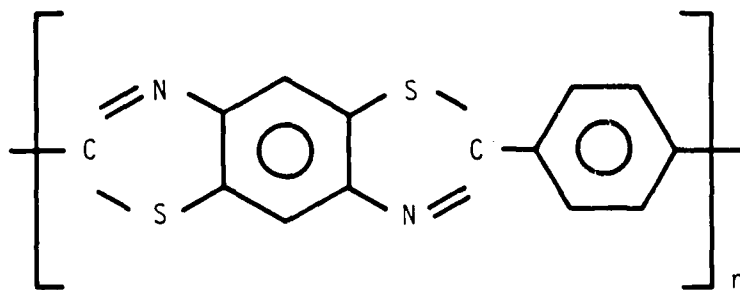


Figure 1. PBT - Poly(p-Phenylene Benzobisthiazole)

Table 1. Comparison of Fiber Properties

Property	PBT	Kevlar 49®	High Strength Carbon	High Modulus Carbon
Density (lb/in. ³)	0.05500	0.052	0.063	0.063
Tensile strength (psi)	500x10 ³	400x10 ³	460x10 ³	270x10 ³
Strain at break (%)	1.5	2.5	1.3	1.3
Specific tensile strength (in.)	9.1x10 ⁶	7.7x10 ⁶	7.3x10 ⁶	4.3x10 ⁶
Modulus (psi)	50x10 ⁶	18x10 ⁶	36x10 ⁶	75x10 ⁶
Specific Modulus (in.)	9.1x10 ⁸	3.5x10 ⁸	5.7x10 ⁸	12x10 ⁸
Compressive strength (psi)	~50x10 ³	~40x10 ³	460x10 ³	270x10 ³
Coefficient of thermal expansion, (ppm/°C)	-5	-1.1	-0.4	-0.4
Thermal conductivity, / (W/m-K°)	0.28/0.065	3.1/0.33	20	20
Dielectric constant	~3	3.7	*	*
Maximum Temperature (°C)	over 600°C	300°C	over 1000°C	over 1000°C
*Conductor.				

Table 2. Comparison of Film Properties

PBT film*				
Property	Achieved	Projected	Polyester*	Polyimide
Density (lb/in. ³)	0.055	0.055	0.050	0.051
Tensile strength machine direction (psi)	280x10 ³	400x10 ³	45x10 ³	25x10 ³
Cross machine direction	20x10 ³	40x10 ³	25x10 ³	25x10 ³
Strain at break (%)	2	2	40	70
Tensile modulus (psi)	15x10 ⁶	30x10 ⁶	0.8x10 ⁶	0.43x10 ⁶
*Oriented in machine direction.				

Table 3. The Fiber and Film-Forming

1. Preparation of dope	Isotropic or unoriented nematic solution
2. Extrusion through die	Solution of oriented rods
3. Extension of air gap	Solution of oriented rods
4. Coagulation	Liquid-solid transition
5. Post treatment (drying, heat treatments)	Oriented solid

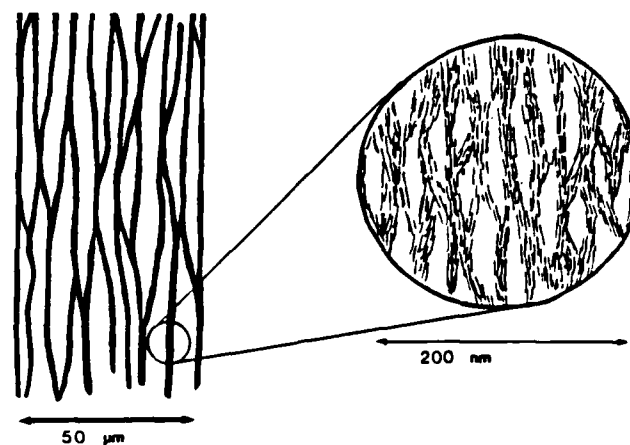


Figure 2. Structural Model for the Coagulated (Wet) PBT Fiber

PBT films can be processed so that the rod-like molecules will lie in the plane of the film, and will be oriented in more than one direction (biaxial orientation) as shown in Figure 3.

Biaxially-oriented PBT films have been produced with a range of longitudinal (machine direction) and transverse strengths, depending on the orientation angle and the relative volume of oriented materials (5). Just as a composite material depends on the orientation of the plies, the bulk properties of a PBT film interpenetrating network (IPN) depend on the orientation of the rod-like molecular microstructure, and properties of the IPN. From work with PBT fibers, we know that the coefficient of thermal expansion (CTE) in the fiber direction is low and negative (less than $-1 (10^{-6}) ^\circ\text{C}^{-1}$, similar to Kevlar and graphite fibers) and that the transverse fiber CTE is positive and higher. Depending on the material properties (CTE, stiffness, Poisson's ratio, etc.), we believe the overall CTE of the film can be altered by selection of IPN properties and orientation of PBT microstructure.

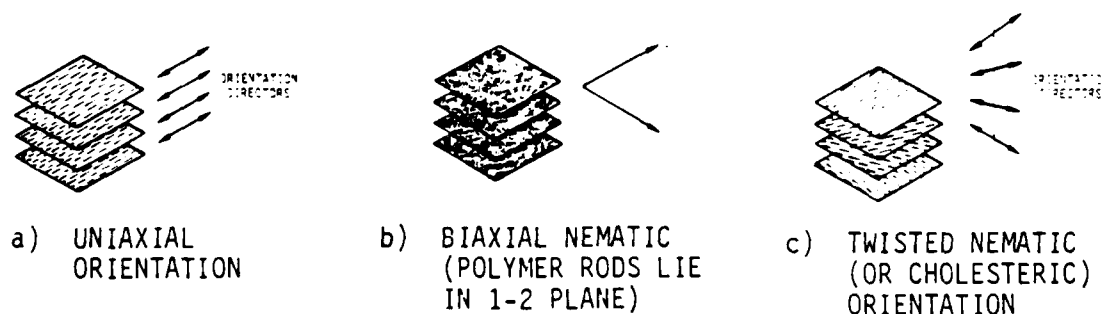


Figure 3. Morphology of Oriented PBT Films

2.2 PBT/Sol-Gel Glass IPNs

The major problems confronting PBT film-based composites are low compressive strength and interlaminar adhesion. A PBT/glass "microcomposite" has the potential of solving these problems and providing additional properties contributed by the glass infiltrant. The compressive strength of PBT fibers is known to be low compared with tensile properties. This is attributed to buckling of the fibrillar network, as evidenced by kinked regions (see Figure 4). These kinked regions regain about 90 percent of their original tensile strength upon re-tensioning, according to researchers.

"Micro-buckling" appears to be the cause of low compressive strength in fibers, and is likely to be observed in films. If the fibrillar network (which results from processing ordered polymers) could be filled with a high compressive strength material such as glass, buckling of the network could be constrained, thereby greatly improving the composite compressive strength. However, the glass provides a means for bonding films into laminates since it would be mechanically interlocked with the PBT microstructure.

The fibrillar microstructure of PBT films (and fibers) is key to forming a PBT/glass microcomposite, and is the result of processing liquid crystalline solutions of PBT, as outlined below:

1. Oriented films are extruded, stretched, sheared, etc. from a nematic (liquid crystalline) low concentration polymer solution, or spinning dope, of PBT in poly (phosphoric acid).
2. The oriented dope is coagulated with water causing deprotonation of the rod-like molecules, giving rise to an interlocked PBT network filled with water and acid.
3. After a period of time the acid is washed out by diffusion, leaving a water-swollen PBT fibrillar microstructure.
4. Water is removed by evaporation, and under proper constraint the PBT film will densify to form a high quality film.

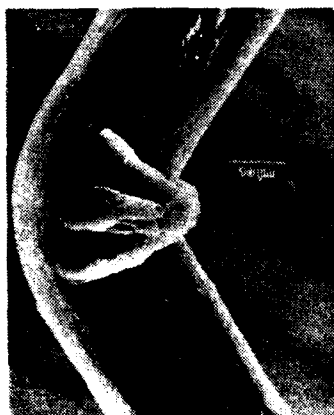


Figure 4. SEM Micrograph of Compressive Failure of a PBT Fiber
(from *Macromolecules*, 1981, 14, 1135)

Upon tensile testing, the PBT films rupture and the fibrillar network is evidenced by thread-like strands at the fracture surface (see Figure 5).

We have infiltrated the water-swollen fibrillar PBT network (which results at Step 3 above) with a glass matrix produced by specially adapted sol-gel processing. Subsequent drying and densification produced PBT/glass microcomposite materials.



Figure 5. Fracture Surface of PBT Film

2.3 PBT/Sol-Gel Glass IPN Formation

Sol-gel processing is still in the early stages of development and exploitation. Its greatest advantages here are:

- The chemical precursor used to form "polymeric" gels can easily infiltrate the swollen PBT film and form a homogeneous IPN of PBT microfibrils and sol-gel glass
- A number of borosilicate glass compositions are known to densify in the 400° to 500°C range, well within the limits of PBT. The ability to densify the PBT/glass was demonstrated early in the program.

The potential for integrating sol-gel glass processing with current PBT processing becomes immediately evident from a brief overview of sol-gel glasses.

Sol-gel processing of glasses and ceramics involves hydrolysis of low molecular-weight monomeric precursors in solution. The precursor is reacted with water to form a coherent gel. This resulting gel can then be converted to a dense glass or crystalline ceramic by uniaxial or isostatic pressure. Because the gel has a high specific surface area and molecular scale homogeneity, it can be densified at temperatures considerably less than those required for a powder compact and conventional furnace techniques.

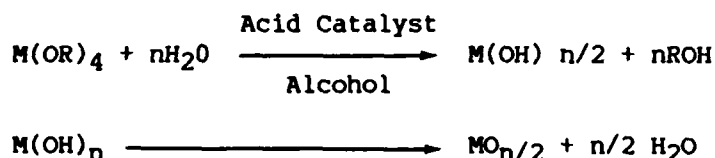
As a result of their inherent microporosity in the water-swollen state, PBT films are uniquely suited for development into novel IPNs, where regions between microfibrils become infiltrated with useful reactive species. Organic silicon alkoxides were chosen as candidate filler precursors, because they hydrolyze in the presence of water to produce rigid silica glasses of high compressive strength and thermal stability. In addition, the chemical

precursors used in sol-gel methods rapidly and homogeneously infiltrate the PBT film network, and show promise for reaching adequate density at ambient or slightly elevated temperature and pressures. During the coagulated water-swollen stage the polymer material is microporous with a high internal void volume. By proper control of the solution chemistry, quench bath chemistry and forming variables, a high degree of control of this microporous network is possible. At this stage it is possible to introduce a wide variety of materials into the internal network structure of the polymer. These introduced materials have a major influence on the physical and chemical properties of the resulting dried combination. These intimate matrices can be thought of as IPNs but on a scale somewhat larger than molecular dimensions. They represent a new class of materials.

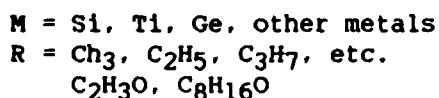
Figure 6 illustrates the structure of the IPN formed upon filtration of water-swollen PBT using sol-gel reagents such as tetraethoxysilane.

The precursors used to prepare the gel can be one of three types: an inorganic salt, a colloidal oxide powder (6-7) or an organometallic monomer (8-9). The organometallic monomers have received much recent attention and are of primary significance to our study. Monomer precursors generally are metallic alkoxide compounds which are commercially available for final glass oxide compositions such as SiO_2 , B_2O_3 , TiO_2 and SrO_2 .

The monomer alkoxide precursors are first polymerized to a "gel" state, in an organic solvent, typically alcohol. The generally accepted chemical reaction is shown below:



where



The resulting "polymeric" gel can consist of linear chains or cross-linked networks, depending upon alkoxide, water, and acid catalyst concentrations (10).

Heat and pressure are used to convert the gel to a glass. During this process, volatiles are evaporated (in addition to those released during drying), and the porous structure is densified by pressure and sintering. At very high temperatures and pressures, the glass may crystallize, but this is not significant to the program effort. The time, temperature, and applied pressure required for desired properties depend upon glass composition. Mixtures of different alkoxides are possible. They should yield lower densification temperatures in the range of 400° to 500°C and industrially practical processing conditions.

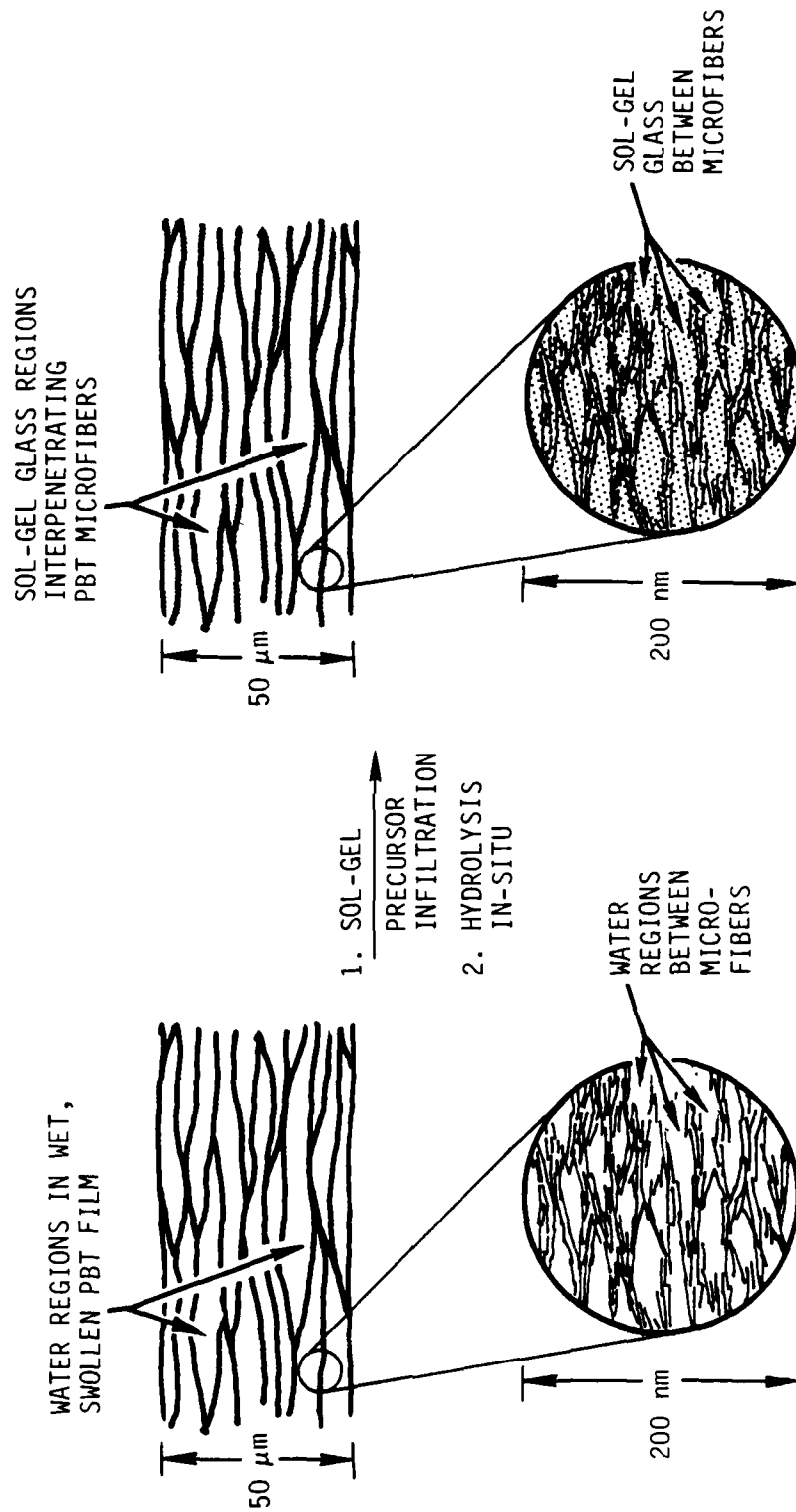


Figure 6. Structure of PBT/Sol-Gel Glass IPN Microcomposite Films

That a fully densified glass phase was not required for development of improved mechanical properties (compressive strength, toughness, CTE), was indicated by improvements in flexural modulus of sol-gel infiltrated PBT films.

3. PBT/SOL-GEL GLASS MICROCOMPOSITE FILMS

A major objective of the Phase I work was to produce a PBT/sol-gel glass microcomposite with the tensile strength, stiffness and toughness of a PBT rod-like polymer, the compressive strength of glass, and the capability to make multilayer film structures. Since both PBT and sol-gel glass are processed from solutions, they provide a unique combination forming a two-phase material with homogeneity on a very fine scale (less than one micron). Foster-Miller, Inc. (FMI) has succeeded in developing processing techniques for making PBT/sol-gel glass films using methods and methods which are practical for further scale-up. The microcomposite films can be readily laminated (subsection 3.3), and possess the desired combination of PBT rod-like polymer and glass properties (subsection 3.4).

This subsection will present:

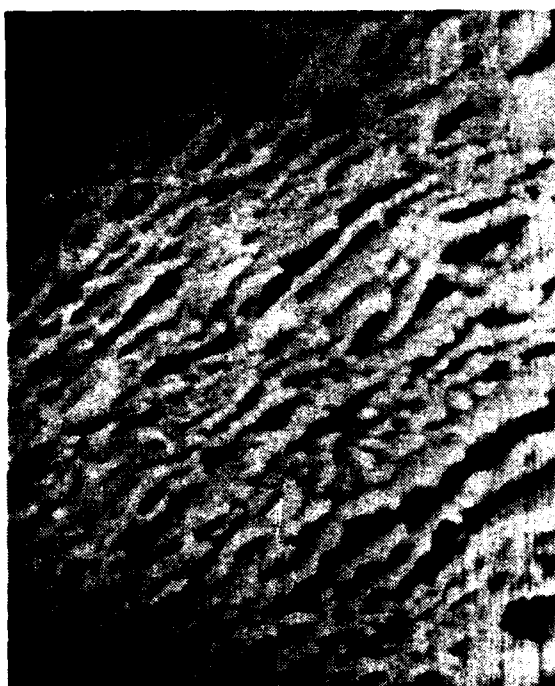
- The general procedures used to prepare microcomposite films
- The process employed to select the sol-gel reagents
- Details concerning infiltration of PBT film with specific reagents
- Properties achieved with single layer sol-gel infiltrated films.

3.1 Microcomposite Film Preparation Procedures

This subsection describes the techniques developed for infusing sol-gel glass reagents into wet, coagulated PBT films. This is the essence of microcomposite processing, since it involves the formation of the sol-gel glass network within the microfibrillar PBT network. Microcomposite film preparation procedures are also the basis for lamination and fabrication of structural composites.

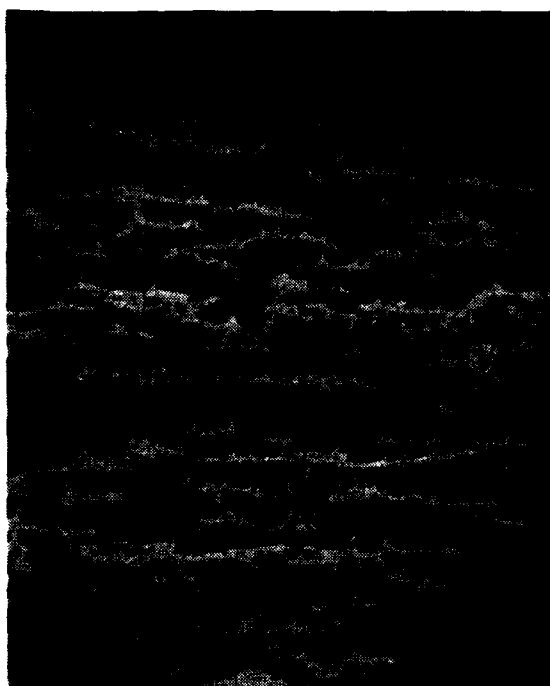
The key starting material for the microcomposite is biaxially oriented, wet, coagulated PBT film (see step 4 in Table 3). This wet PBT film is extruded from relatively high molecular weight, high concentration PBT solutions supplied by SRI International. (The PBT solution (dope) used on the Phase I program was designated SRI code 5103-28, 40 Intrinsic Viscosity 13.7 percent solids by weight.) PBT film thus prepared was fully washed of residual solvent and stored under neutral water until use. The SEM photograph in Figure 7 illustrates the microfibrillar nature of PBT film. In this photomicrograph, a water-swollen PBT film has been frozen in liquid nitrogen, then brittle-fractured perpendicular to the machine-direction, fracturing the film into bundles of microfibrils, less than 200 nm (0.2 μ) in size. This appears to be the approximate scale of the PBT microfibrillar network; additional work is required to fully characterize its dimensions.

Two different techniques were utilized to introduce sol-gel reagents into PBT films; namely, direct diffusion of reagent solutions with water-swollen films and infiltration of alcohol-swollen films with subsequent hydrolysis steps. Details concerning each procedure are presented below.



1 μ

Figure 7a. Edge View of Frozen, Water-Swollen PBT Film Fractured Perpendicular to Machine-Direction, Magnification = 10,000X



1 μ

Figure 7b. Edge View of PBT/Sol-Gel Glass Film (50% SiO₂) Fractured Perpendicular to Machine-Direction, Magnification = 10,000X. The Sample had been Densified at 300°C/1000 psi

- Infiltration and Direct Reaction of Water-Swollen PBT Films - Sol-gel reagents were diluted to various concentrations using methanol solvent. Water-swollen PBT films, in circular frames, were immersed in the corresponding sol-gel solutions for 24-hr periods. During that time, reagent diffused into the microporous interiors of the films, reacting with water and traces of phosphoric acid present to form sol-gel glass networks throughout the films, as shown in the left side of Figure 8.

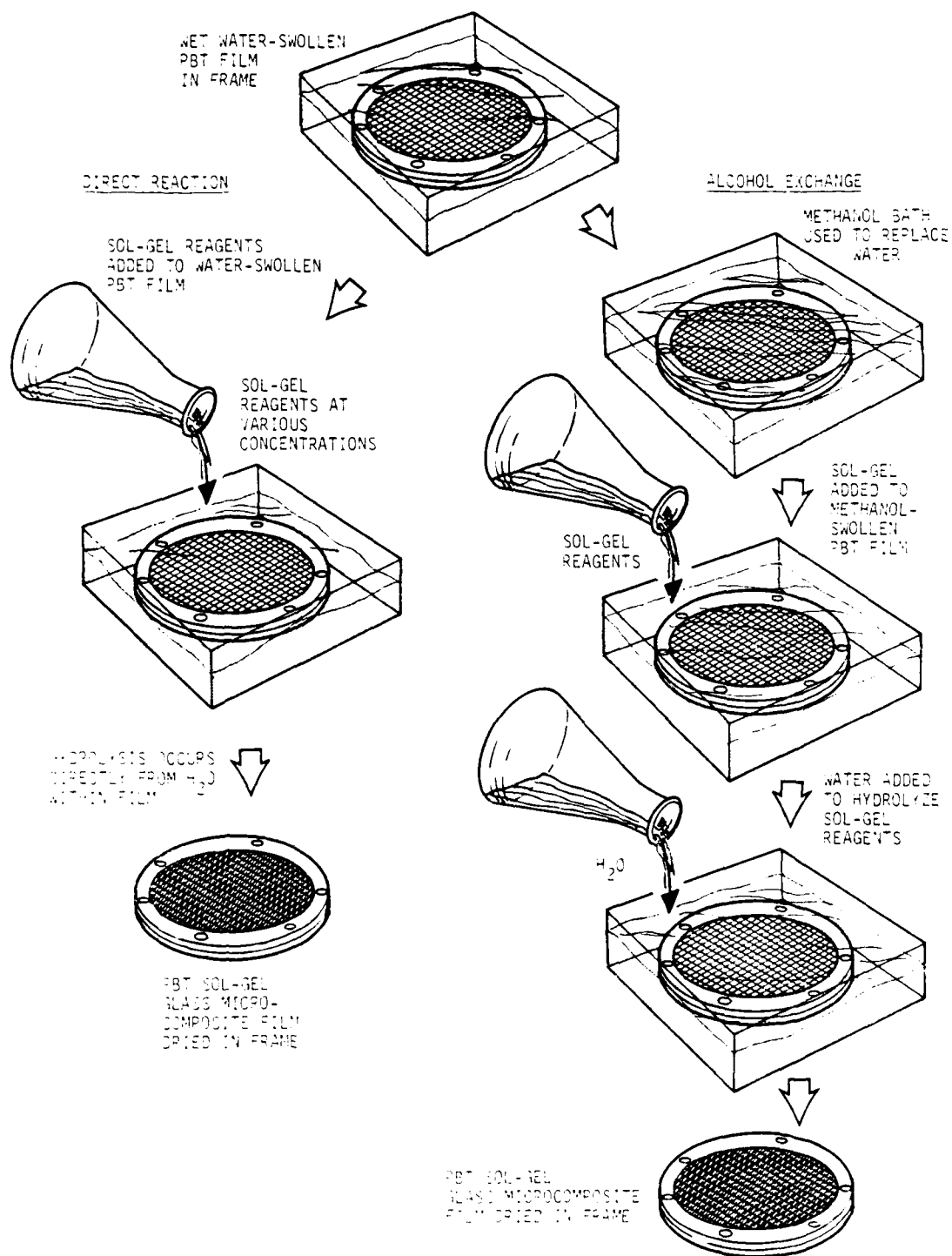


Figure 8. Two Methods were Used to Process PBT/Sol-Gel Glass Microcomposite

- Sol-Gel Infiltration of Alcohol-Exchanged PBT Films - In this procedure, shown schematically in Figure 8, the water in water-swollen PBT films was exchanged with methanol in stages, to prevent collapse of the swollen network. Thus, water-swollen PBT films were immersed in separate methanol solutions containing 75, 50, 25, and 0 percent water respectively, for 8-hr periods, in order to affect complete alcohol exchange within the films. Methanol-swollen films were then infiltrated with sol-gel reagent solutions and subsequently removed and placed into distilled water to affect hydrolysis within the films, or, as previously described, infiltrated with sol-gel reagents containing water, catalyst and reactive resin components.

Although alcohol-exchange procedures for sol-gel reagent infiltration were tedious and time-consuming, they provided the greatest control over sol-gel glass formation and composition. In addition, the technique allowed infiltration of water-insoluble or water-deactivated reactive resins.

The two techniques above provide important processing alternatives to control the PBT/sol-gel glass microstructure, resulting physical properties, and full-scale fabrication options. Both were used in the Phase I program, and both are recommended for further work in Phase II. Their particular advantages and uses will become apparent through discussions in later subsections.

The final step shown in Figure 8 is drying. It is the same for both direct reaction and alcohol-exchange techniques, and produces dense, free-standing PBT/sol-gel glass films. Drying removes unreacted alkoxide, residual water and alcohol, in addition to densifying the PBT/sol-gel glass microcomposite. Previous research at FMI involving PBT film, indicated the need for stepwise heating to 250°C to remove tightly-bound water and prevent blistering. We applied similar procedures to the drying of sol-gel/PBT microcomposites, thereby obtaining specimens of excellent quality.

In some instances, films were not dried. Instead of proceeding directly to the drying step, wet PBT/sol-gel glass films were removed from the frames shown in Figure 8. Thus, either dried or wet films could be used in subsequent lamination methods, as described in subsection 3.3.

3.2 Selection of Sol-Gel Reagents

Sol-gel reagents were selected according to the following criteria:

- Ability to infiltrate PBT efficiently, to high loadings
- Capability of hydrolyzing in-situ, forming useful products (rigid glass, elastomers, glass containing reactive pendant groups)
- Suitability for scale-up including ease of processing and availability.

Initial screening included evaluation of six different organo-functional sol-gel reagents to facilitate selection of the best candidate for extensive evaluation and to determine changes imparted to PBT film by infiltration with various sol-gel glass compositions.

The sol-gel infiltration technique involving direct infiltration of water-swollen PBT films was utilized whenever possible, because of its convenience and effectiveness in introducing high loadings of sol-gel glass within PBT films.

Table 4 lists the sol-gel reagents that were infiltrated into PBT films to high loadings. The ratio of PBT to glass was controlled by concentration of the reagent.

Table 4. Sol-Gel Reagents Infiltrated into Microfibrillar PBT Film

<u>Reagent</u>	<u>Potential Application</u>
Tetramethoxysilane (TMOS)	Rigid glass-filled PBT
Tetraethoxysilane (TEOS)	Rigid glass-filled PBT
Glycidyoxypropyl-trimethoxysilane (GPTMOS)	Formation of PBT/sol-gel glass/epoxy resin IPN microcomposite
Methacryloxypropyl-trimethoxysilane (MPTMOS)	Formation of PBT/sol-gel glass/polymethylmethacrylate IPN microcomposite
Methyltrimethoxysilane (MTMOS)	Organically modified, glass-filled PBT "toughened" microcomposite
Dimethyldimethoxysilane (DMDMOS)	Siloxane elastomer-filled PBT microcomposite

TMOS was chosen as the candidate for extensive evaluation because this reagent was readily available, infiltrated water-swollen PBT to loadings greater than 50 percent by weight, and reacted rapidly to form rigid, PBT/silica IPNs that densified partially upon heating to 250°C under pressure. Results obtained for TMOS can be qualitatively applied to other sol-gel formulations, thus it served as a model material for the Phase I study.

3.3 Single Layer PBT/Sol-Gel IPN Films

Single layer PBT/sol-gel microcomposites were prepared by sol-gel reagent infiltration of water-swollen PBT films in order to determine the effect of various sol-gel reagents upon film properties. Reagents were varied in such a way as to form rigid silica, organically-modified glass, and siloxane elastomers, within microporous interiors of PBT films. Control of sol-gel reagent concentration and type provided PBT/sol-gel IPN microcomposite films that varied in properties from soft, flexible and tough to rigid and brittle. Details concerning the infiltration of various sol-gel reagents into PBT film are presented below.

TMOS was chosen as the prime candidate for infiltration into PBT films, since this reagent reacts with controlled amounts of water to form rigid gels, which densify upon slow drying into clear, continuous monolithic silica glasses. This process was shown earlier on the left side of Figure 8, and the chemistry is shown in Figure 9.

Infiltration of TMOS into water-swollen PBT films produced rigid PBT/silica glass microcomposites which densified upon heating to 300°C under pressure.

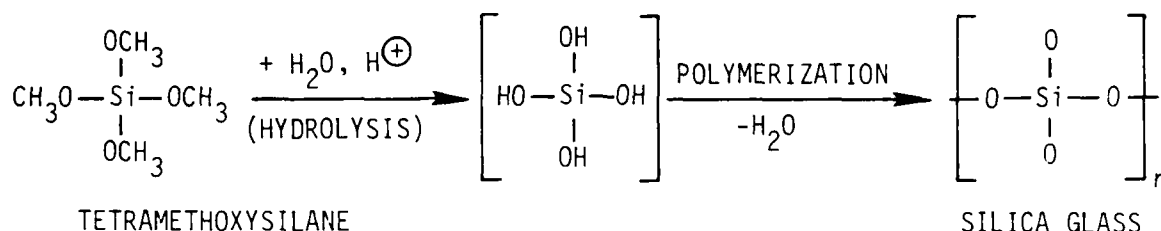


Figure 9. Hydrolysis of TMOS to Sol-Gel Glass

DMDMOS was tested, since hydrolysis of this reagent produces dimethylsiloxane elastomeric polymers (silicones), providing a method for introduction of elastomeric materials into the microporous network of PBT film. Figure 10 illustrates the hydrolysis reaction.

DMDMOS hydrolyzed within PBT film interiors to form PBT/siloxane elastomer microcomposite films that were flexible and smooth to the touch. Elastomer-infiltrated PBT films are expected to exhibit superior ballistic impact properties.

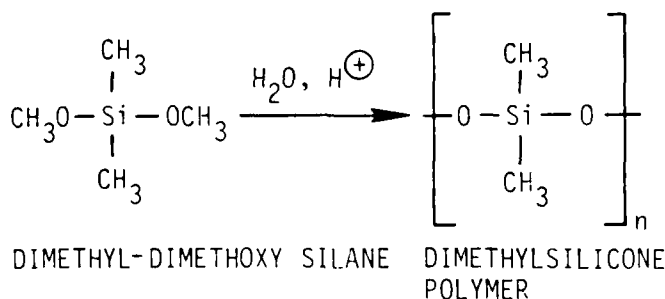


Figure 10. Hydrolysis of DMDMOS to Silicone Elastomer

MTMOS hydrolyzed to a rigid glass containing pendant organic groups which contributed unique properties to the glass, such as improved toughness. Figure 11 illustrates the reaction.

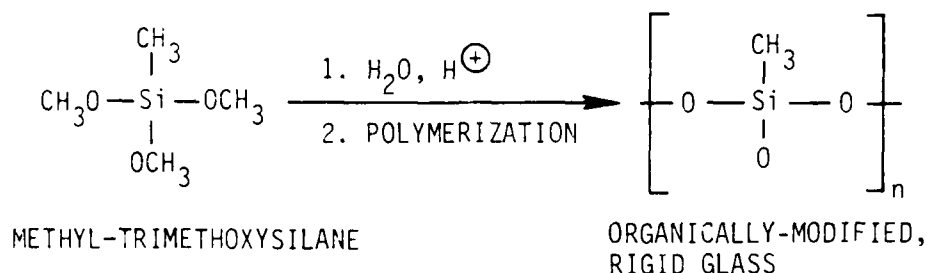


Figure 11. Hydrolysis of MTMOS to an Organically-Modified Sol-Gel Glass

3-GPTMOS produced PBT/sol-gel glass microcomposites containing pendant epoxy groups on silicon atoms. Addition of epoxy resin to epoxy-containing sol-gel compositions before infiltration will provide "epoxy resin-toughened" sol-gel glass/PBT microcomposites, with epoxy groups on silicon chemically bound to an epoxy matrix. Figure 12 illustrates the formulation of epoxy resin/sol-gel glass compositions.

Compositions illustrated above would be useful as adhesives for binding PBT films into multiple layer laminates. Material infiltrated into the film would improve interlaminar shear strength of the composite by adhering microfibril layers together.

Treatment of PBT films with GPTMOS prior to lamination with epoxy resins should also significantly improve the mechanical properties of consolidated laminates.

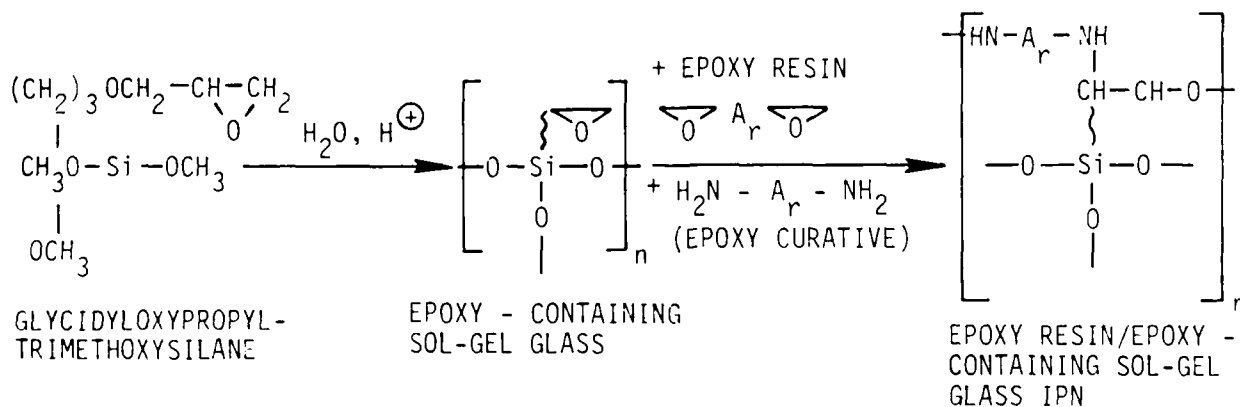


Figure 12. Formation of Epoxy Resin/Epoxy-Containing Sol-Gel Glass IPN

3-MPTMOS was combined with TEOS and catalyzed methylmethacrylate (MMA) monomer, according to a procedure suggested by Professor Pantano. Figure 13 illustrates the reaction, which formed an IPN of polymethylmethacrylate (PMMA) within a sol-gel glass.

This sol-gel reagent was infused into alcohol-swollen PBT films by the process shown on the right side of Figure 8. This produced PBT/methacrylate-functional sol-gel glass/MMA monomer film compositions which polymerized upon heating to PBT/sol-gel glass/PMMA microcomposites with IPN components chemically bonded to each other.

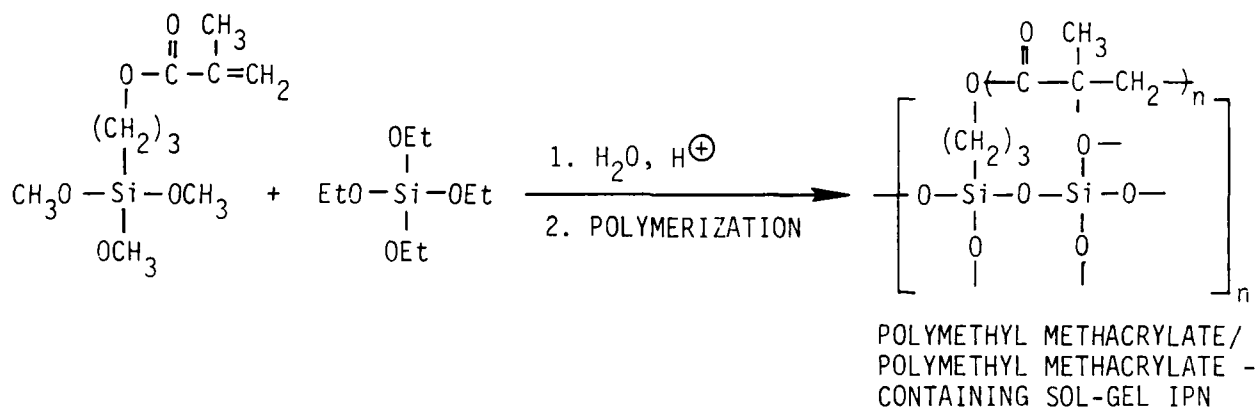


Figure 13. IPN Containing PMMA/PMMA-Containing Sol-Gel Glass

3.4 Properties of Single Layer Sol-Gel-Infiltrated PBT Films

Although water-swollen PBT films decreased in thickness upon drying, sol-gel infiltrated films retained significant fractions of their original thickness. Evidently, the presence of sol-gel glass between microfibrils inhibited collapse of the swollen networks upon drying. PBT/sol-gel glass microcomposite films were therefore of greater thickness than untreated films. However, PBT/sol-gel glass microcomposite films were readily densified by compression at elevated temperatures. For example, consolidation of 100 percent TMOS sol-gel reagent-infiltrated PBT films at 300°C and 1000 psi pressure decreased film thickness from 0.007 to 0.005 in., and increased flexural stiffness, as indicated by changes in three-point bending modulus from 1.06×10^6 to 4.1×10^6 psi following densification. Further densification at temperatures approaching 500°C did not significantly decrease film thickness. However, color of the film had changed from brown to greenish-gold.

Table 5 illustrates the effect of sol-gel glass infiltration on PBT film properties.

Table 5. Properties of Sol-Gel Glass-Infiltrated PBT Films

Sample	Description ^a	Thickness (in.)	Appearance	Weight ^b & SiO ₂ Pyrolysis Residue	Three-Point ^c Bending Modulus (psi x 10 ⁶)
1	Untreated PBT film	0.004	Flexible, tough	0	0.11
2	PBT film stage-dried to 250°C	0.0028	Stiffer than sample 1, tough	0	1.7
3	PBT film heat-treated to 450°C (nitrogen)	0.002	Darkened, slightly embrittled	0	2.0
4	PBT film treated in 25% TMOS	0.0036	Flexible, tough, smooth surface	Traces of white residue	0.14
5	PBT film treated in 50% TMOS	0.004	Stiff, some- what brittle	17 (8)	0.84
6	PBT film treated in 100% TMOS	0.007	Very rigid, brittle, rough	47 (22)	1.06
7	PBT film treated in 100% DMDMOS	0.005	Flexible, tough smooth surface	23 (11)	0.19
8	PBT film treated in 100% MTMOS	0.006	Rigid, brittle rough surface	50 (23)	0.94
9	PBT film treated in 100% GPTMOS	0.005	Flexible, tough, smooth	13 (6)	(not measured)
10	Sample 6 densified at 300°C/ 1000 psi	0.005	Very rigid, smooth, brittle	47 (22)	4.1

^aSamples were air-dried under tension at room temperature unless otherwise indicated.

^bSamples were pyrolyzed at 600°C in air, leaving continuous, transparent residues of silica.

^cThree-point bending modulus was determined using a modification of the ASTM 0790 three-point bending test on free-standing films.

Pyrolysis of PBT/sol-gel films in air yielded continuous, translucent silica residues, providing evidence that continuous, IPNs of glass had been present within sol-gel glass-infiltrated PBT films. PBT film flexural stiffness increased as the amount of sol-gel glass infiltrant increased (samples 4, 5, and 6). Densification of PBT/sol-gel glass IPN films under moderate conditions of temperature and pressure (300°C/1000 psi) decreased film thickness by as much as 30 percent and significantly increased the flexural bending modulus (sample 10). Infiltration of elastomeric silicone into PBT film (sample 7) did not significantly increase the bending modulus as compared to the control (sample 1). The details of the three-point flexure test and other material characterization tests are explained in subsection 3.4.

4. PBT/SOL-GEL GLASS LAMINATES, COATINGS AND MONOLITHS

To provide useful materials with broad application, PBT/sol-gel films must be processed into structural shapes. To this end we explored the preparation of laminates and monoliths. We also investigated the potential for coating PBT films with sol-gel materials to improve such important surface properties as atomic oxygen resistance, laser radiation resistance, and ability to form adhesive bonds.

The lamination procedures and results achieved with several sol-gel glass compositions are described below, followed by brief discussions of monolith fabrication and coating procedures.

4.1 PBT/Sol-Gel Glass Laminates

Techniques employed to laminate PBT/sol-gel glass microcomposite films included the following:

- Lamination using epoxy resin as adhesive - In this technique, stage-dried, PBT/TMOS glass microcomposite films were coated with high temperature epoxy resin, then laminated under heat and pressure to cure the resin. Dense, well-consolidated laminates were prepared that exhibited improved resistance to delamination compared to similar specimens prepared from untreated PBT film.
- Lamination using reactive monomer-containing sol-gel reagents as adhesive - This method involved infiltration/coating of PBT films with sol-gel reagents that contained reactive monomers, such as MMA. Lamination of multiple plies of sol-gel precursor infiltrated PBT film under heat and pressure gave rise to sol-gel glass formation and monomer cure, providing well-consolidated, PBT/sol-gel glass/MMA composites of high interlaminar adhesive strength. The presence of PMMA limits the use temperature of such laminates. However, application of similar techniques using epoxy-functional sol-gel reagents with epoxy resin monomer will provide composites which exhibit outstanding properties at elevated temperatures. Figure 12 in subsection 3.2.3 illustrates the formation of epoxy resin-containing sol-gel IPNs.
- Lamination using sol-gel glass as adhesive - In this method, alcohol-swollen PBT films were first infiltrated and coated with TEOS/ethanol/H₂O/HCl sol-gel compositions. Reagent-swollen films

were then pressed together and the temperature slowly raised in stages to 500°C to affect fusion of sol-gel glass and consolidation of the laminate.

The three lamination procedures described above are discussed in greater detail below.

4.1.1 Lamination of PBT/TMOS Sol-Gel Glass Microcomposite Films Using Epoxy Resin

Stage-dried, PBT/TMOS sol-gel glass microcomposite films were coated on each side with degassed BPA epoxy resin containing MMA curative and stacked in a mold. The 12-ply PBT/sol-gel/epoxy laminate was cured at 150°C/1000 psi for 4 hr before cooling under pressure. Removal of sample revealed a well-consolidated PBT/sol-gel microcomposite film laminate that exhibited higher stiffness than a control PBT laminate and resisted delamination from within PBT film plies upon flexing.

Sol-gel treatment of PBT film has therefore improved the cohesion between plies in a laminate using epoxy binder resin. Application of epoxy-containing sol-gel reagents to PBT laminate fabrication should significantly improve interlaminar adhesion, since epoxy groups in the matrix will bond chemically to the glass in an IPN of PBT/sol-gel glass/epoxy resin.

4.1.2 Lamination Using MMA-Containing Sol-Gel Reagent as Binder

This procedure, recommended by Dr. Pantano, included the following steps:

1. Alcohol-exchange, shown previously, was used. This step was required in the experiment to allow infiltration of functional sol-gel reagent containing reactive monomer.
2. Ethanol-swollen PBT films were immersed in a sol-gel solution containing TMOS, MPTMOS, water, ethanol and traces of 0.1M HCl.
3. The temperature was raised to 60°C for 1 hr.
4. MMA monomer containing 0.1 percent benzoyl peroxide catalyst was then added and temperature raised to 80°C.
5. One half of the solution was distilled off over a 3-hr period.
6. Sol-gel-swollen/coated PBT films were removed from the stretch frames, then four plies were stacked within a mold, as illustrated in Figure 14. Frame-holders were no longer needed as the mold constrained the film plies.
7. The mold was heated to 100°C under 1000 psi pressure for 1 hr, then cooled under pressure.
8. Removal of the four-ply PBT/sol-gel microcomposite laminate provided a clear, transparent, well-consolidated sample that did not delaminate upon flexing.

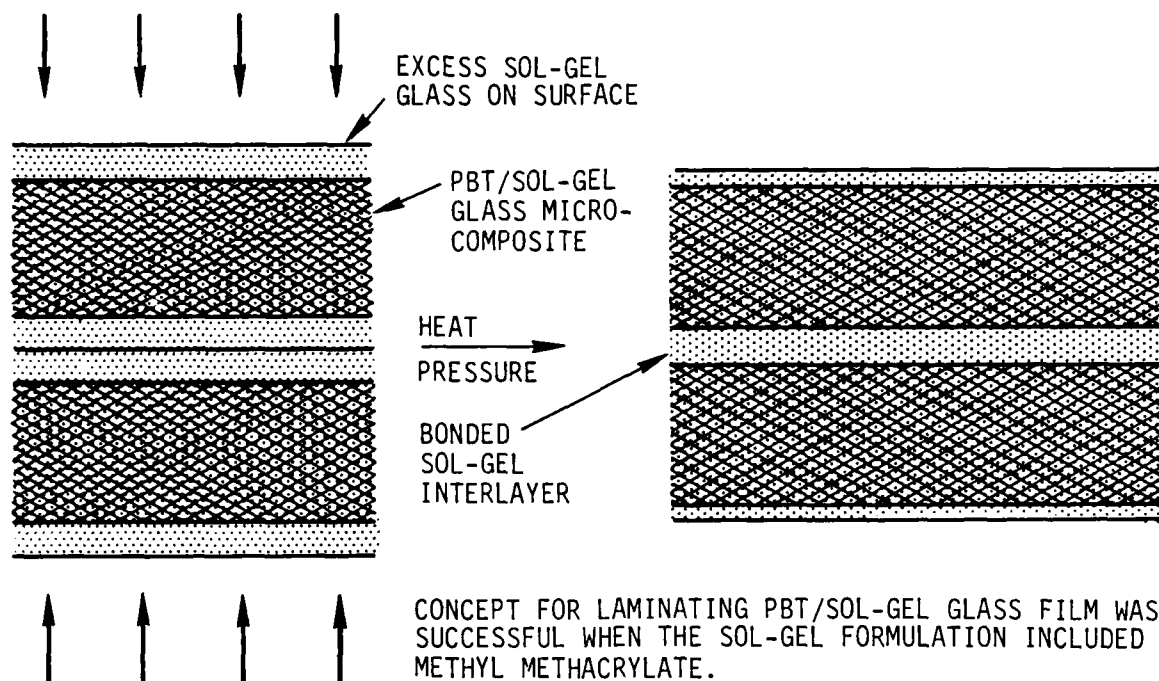


Figure 14. Concept for Laminating PBT/Sol-Gel Glass Film was Successful When the Sol-Gel Formulation Included MMA

4.1.3 Lamination Using TMOS Sol-Gel Reagent as Binder

Alcohol-exchanged PBT films were infiltrated with sol-gel reagent composed of ethanol: TEOS:H₂O:HCl in the ratio, 1.0:0.1:1.0:0.01, respectively. Alcohol-exchange was required in this experiment to allow infiltration of preformulated sol-gel reagent, containing sufficient water and HCl catalyst for subsequent conversion to glass. Films thus prepared were then removed from solution, immediately stacked into 12 multiple plies, then compressed at 500 psi at room temperature for 24 hr. Pressure was maintained while the temperature was raised to 500°C in stages. Inspection of the laminate after cooling to room temperature under pressure revealed that it exhibited low interply adhesion. Individual plies were easily peeled apart. It is possible that consolidation temperatures had not exceeded sol-gel glass fusion temperatures. More work is required to evaluate this technique with sol-gel formulations which will densify at relatively low temperature and pressures.

4.2 Sol-Gel Glass Coatings on PBT Films

Sol-gel glass precursor solutions were applied to the surfaces of stage-dried PBT films by multiple dipping techniques, in order to demonstrate the capability of depositing tenacious, crack-free protective coatings on PBT film surfaces. Sol-gel glass coatings on PBT/sol-gel glass microcomposite structures will improve such critical properties as atomic oxygen resistance, abrasion-resistance, and laser-resistance. Two sol-gel coatings were evaluated:

- Dimethylsiloxane Elastomer Precursor Sol-Gel Coatings - Elastomeric coatings containing mixtures of TMOS, DMDMOS, water and acid catalyst were applied to the surfaces of stretched, stage-dried, PBT films by multiple dipping. Oven-drying provided tenacious, transparent, thin film coatings that did not crack or peel. PBT films were therefore successfully coated with films of sol-gel glass.
- Methacrylate-Containing Sol-Gel Coatings - Solutions containing MMA, TEOS, ethanol, water and methacrylate-functional sol-gel reagent prepared in subsection 3.3.1.2 of this proposal were coated on stretched, stage-dried PBT films by multiple dipping techniques. Oven-drying of the coatings provided clear, transparent, tenacious films that did not crack or peel.

4.3 PBT Film-Embedded, Sol-Gel Monoliths

Monolithic, transparent sol-gel glass castings containing PBT/sol-gel IPN films embedded within the glass were prepared in order to demonstrate the capability of producing PBT film-toughened, sol-gel glass articles. Dimethyl formamide (DMF) drying control additive was used to reduce the tendency of monoliths to crack during lengthy drying steps.

Details concerning the casting of PBT film-embedded sol-gel glass monoliths are presented below.

Methanol-swollen PBT films were immersed in sol-gel reagent solutions composed of methanol:TMOS:H₂O:DMF in the ratio, 1.0:1.0:10:1.0, respectively, and reagent allowed to infiltrate the film. Gelation proceeded smoothly within several days, yielding aerogels with PBT films suspended within the gel. Slow drying over a period of several weeks caused densification to occur, as the gels underwent shrinkage, pulling away from the walls of plastic containers. Attempts at this point to increase the evaporation rate of solvent from the aerogels caused cracking to occur within the specimens. Although the monolith samples cracked when attempts were made to accelerate drying, the presence of DMF appeared to significantly improve the drying behavior compared with previous experiments which had not utilized the drying control additive. Figure 15 illustrates the monolith casting procedure.

SOL-GEL REAGENT SOLUTION
WITH INFILTRATED PBT FILM
SUSPENDED WITHIN SOLUTION

SOL-GEL GLASS CONTAINING
SUSPENDED PBT FILM



Figure 15. Procedure for Casting PBT/Sol-Gel IPN Film-Reinforced Sol-Gel Monoliths

5. TESTING AND CHARACTERIZATION

To determine the effect of sol-gel treatment on PBT film properties, PBT/sol-gel glass IPN films were subjected to a variety of testing procedures:

- Tensile strength and modulus were measured to determine the changes in strength and elongation with glass content. Although the modulus did not change significantly for films with moderate glass content, both tensile strength and elongation to break did decrease with increasing glass content
- Three point bending tests indicated significant increases in flexural bending strength and modulus with increasing glass content. Densification of the films at elevated temperatures and pressures further increased the bending modulus. The three point bending behavior of sol-gel glass infiltrated PBT films provided indirect evidence that significant improvement in compressive behavior of PBT films has been achieved
- Flame atomic absorption spectroscopy determined the sol-gel glass content of PBT films infiltrated with various reagents. This provided evidence that PBT films could be readily infiltrated with high loadings of rigid glass or soft elastomer, depending upon the reagent used
- Specific gravity and water uptake experiments provided indications of the extent of porosity within the films
- Thermal gravimetric analysis of PBT/sol-gel microcomposites demonstrated that the superior thermal stability of PBT in air was not affected by inclusion of high sol-gel glass loadings
- CTE measurements of PBT/glass microcomposite films indicated that sol-gel infiltration techniques could be used to control the CTE of PBT structures. This application will be useful in the construction of dimensionally stable structures
- Optical and scanning electron microscopy was utilized to reveal the morphology of sol-gel glass/PBT IPNs. Microscopy of fractured PBT/glass microcomposites indicated that sol-gel reagent had infiltrated throughout microfibrillar regions as well as macroporous regions forming vitreous compositions.

Detailed descriptions of the testing techniques employed and the results obtained are presented in the following subsections.

5.1 Tensile Characterization of Films

Representative samples of the PBT/glass films and PBT "control" films were tested for tensile properties following ASTM D882 standard. Test specimens were 1 in. gage length and 0.2 in. wide. The cross head speed was 0.1 in./min or 10 percent of gage length per minute. Average thickness of the film specimens was measured using a micrometer.

Average tensile strength, modulus and elongation percent of PBT films are compiled in Table 6.

PBT/glass microcomposite films tended to exhibit more glass-like behavior as glass content increased. Tensile strength and elongation-to-break decreased with higher glass content. Modulus remained nearly the same for two lower glass content films. Film A exhibited significantly reduced tensile properties over its control film. The high glass content of 54 percent clearly represents an extreme composition. In general, useful PBT/glass microcomposite films will be infiltrated with controlled glass contents in order to obtain the desired balance in film properties.

The stress-strain behavior reflected this change from the high tensile strength PBT to low tensile strength, high compressive strength glass. Typical stress-strain curves are compared in Figure 16. PBT exhibits an initial high modulus region followed by reduced modulus to break. In contrast, the typical stress-strain curve of the PBT/glass film reflected a more brittle, glassy material. Although the PBT/glass curve initially followed the high modulus behavior of PBT, it fractured at lower loads and extension, reflecting glass-like tensile properties.

This behavior is expected, considering the high tensile strength and stiffness of PBT and the low tensile strength of glass. In tension, the glass is merely taking up space in the PBT film without adding strength. (In compression, however, it is the glass that adds strength.)

Sample C in Table 6 contains about 76 percent PBT by volume and has 82 percent of the original PBT tensile strength. Samples B and A have less PBT load-bearing material and show the trend toward lower tensile strength. The PBT network is still strong in tension and the glass is strong in compression. The ratio of the two must be controlled to achieve desired properties.

Table 6. Tensile Properties of PBT/Sol-Gel Glass Microcomposites

Sample	Preparation	% Weight SiO ₂	% Volume SiO ₂	Tensile Strength (ksi)	Tensile Modulus (Msi)	Elongation (%)
A	100% volume Si(OMe) ₄	54	46	11.7	0.358	1.2
A control	Film dried only	<1	<1	41.5	1.68	4.9
B	50% volume Si(OMe) ₄	36	28	48.2	1.92	2.2
C	25% volume Si(OMe) ₄	30	24	71.0	1.38	5.4
B, C control	Film dried	<1	<1	87.0	1.65	6.2

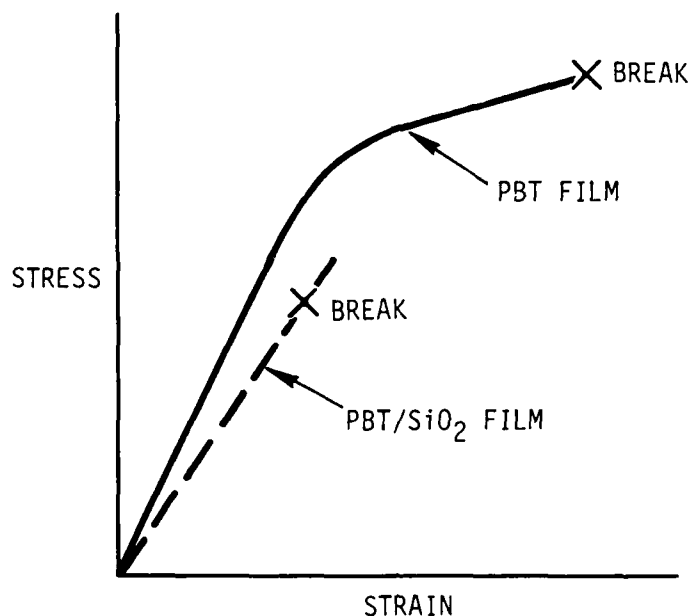


Figure 16. Typical Stress-Strain Curves for PBT Film and PBT/Glass Film

Ideal PBT/sol-gel glass microcomposites will achieve increased compressive strength without unacceptable loss in tensile properties. Tensile data indicates that silica glass contents between 10 to 30 percent by weight produce films with acceptable tensile properties and improved compressive behavior. Adhesive bond strengths of laminates fabricated from these films should also be improved by the presence of sol-gel silica glass/PBT networks.

5.2 Sol/Gel Glass Content

Samples of sol/gel infiltrated PBT film were analyzed for Silicon by flame atomic absorption spectroscopy at Galbraith Laboratories, Knoxville, TN. This technique utilized a Perkin Elmer AA703 and determined Silicon content by weight. Assuming a SiO_2 molecular formula for the glass, estimates for glass content can be made.

The silica content test results of Table 7 and their graphical presentation on Figure 17 indicate that it is possible to control the amount of glass infiltrated into PBT film by varying the sol-gel reagent concentration.

Thus, we believe that the sol-gel reagent hydrolysis reaction under these conditions was significantly slower than the diffusion of alkoxide into the water-swollen film, allowing thorough infiltration into water-swollen PBT films.

This key result is important from the processing perspective. Water-swollen PBT films can be directly infiltrated by Silicon alkoxide sol-gel glass precursor reagents, avoiding the tedious and time-consuming process of alcohol

Table 7. Analytical Silicon Content of Sol-Gel/PBT Films*

Sample	% Silicon	% SiO ₂
100% TMOS-infiltrated PBT	25	54
50% TMOS-infiltrated PBT	17	36
30% TMOS-infiltrated PBT	10	21
25% TMOS-infiltrated PBT	14	30
PBT control	1	2

*Percent Silicon determined chemically at Galbraith Laboratories, Inc. by Atomic Absorption Spectrometry.

exchange prior to sol-gel reagent infiltration. However, alcohol exchange of water-swollen PBT films must be utilized when careful control of infiltrated sol-gel reagent composition is desired and when water-insoluble reactive resins are included in the formulations.

Table 5 in subsection 3.2.4 illustrates silica (SiO₂) residue contents obtained upon pyrolysis of similar PBT/sol-gel glass samples in air. PBT/sol-gel glass film specimens were pyrolyzed at 600°C in air, using an electrically heated kiln. Pyrolysis temperatures were chosen in order to burn

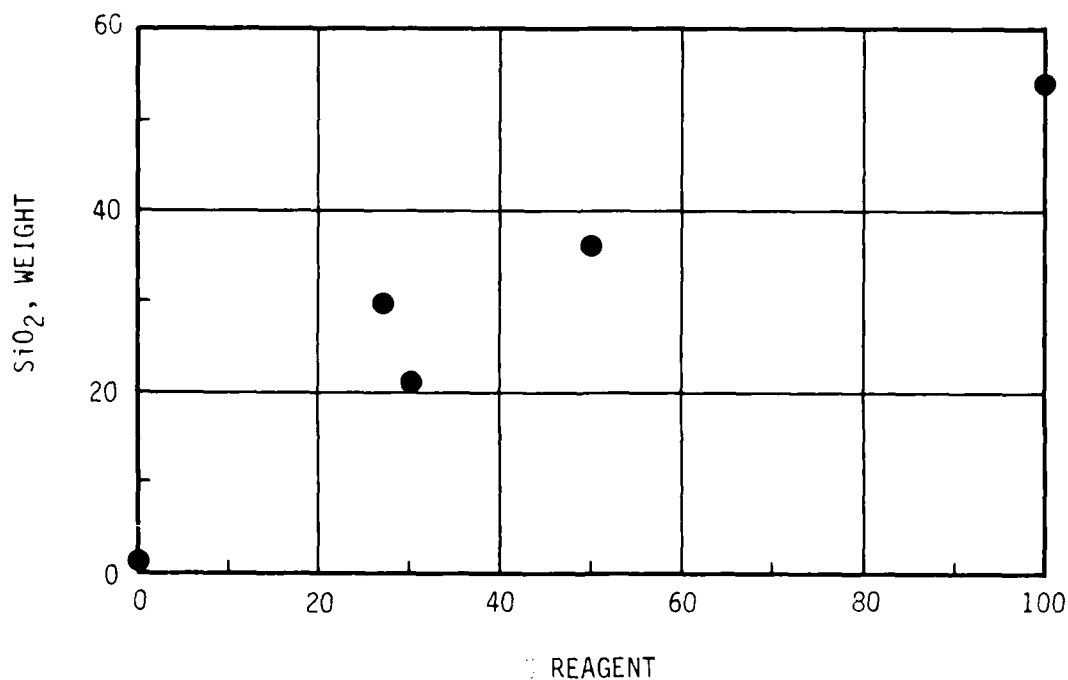


Figure 17. Silica Content of Infiltrated Films by Atomic Absorption Spectroscopy

away organic PBT polymer residues without causing fusion of the fragile, white silica residues. By application of pyrolysis techniques, continuous, transparent, silica residues were obtained that provided evidence of the continuous interpenetrating networks in PBT/sol-gel glass microcomposites.

5.3 Three Point Flexural Bending Modulus of Sol-Gel PBT Films

A modification of the ASTM D790 three-point bending test apparatus was successfully utilized to measure differences in mechanical stiffness for heat-treated and sol-gel-infiltrated, free-standing PBT films. Samples were bent to low degrees of constant deflection by gradual increase in load, in order to remain within linear limits of the bending modulus deflection equation.

$$E_b = L^3 M / 4 b t^3$$

where

- L = span in inches
- M = slope of load/deflection
curve in pounds per inch deflection
- b = sample width in inches (0.5 in.)
- t = sample thickness in inches

Three determinations were made for each sample and an average load value computed. Figure 18 illustrates the test apparatus. Test results are presented in Table 5 in subsection 3.2.4 and illustrated graphically in Figure 19.

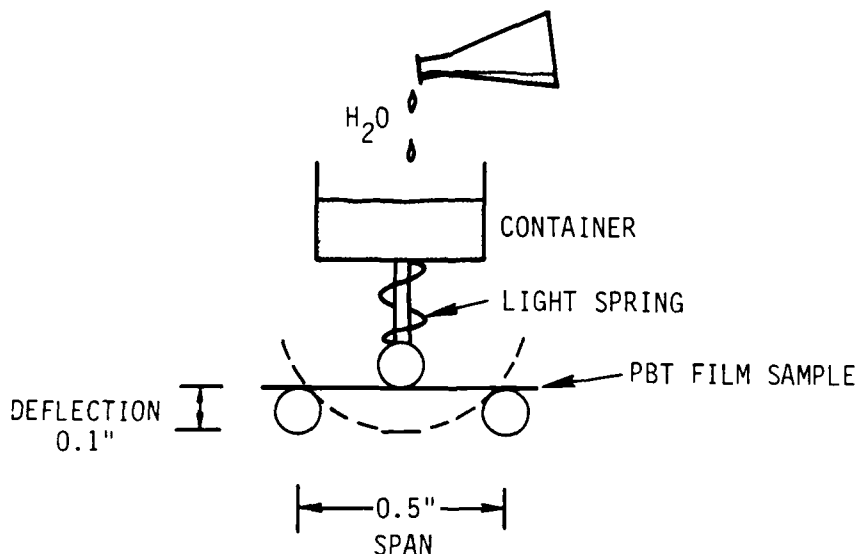


Figure 18. Three-Point Bending Apparatus for Sol-Gel/PBT Films

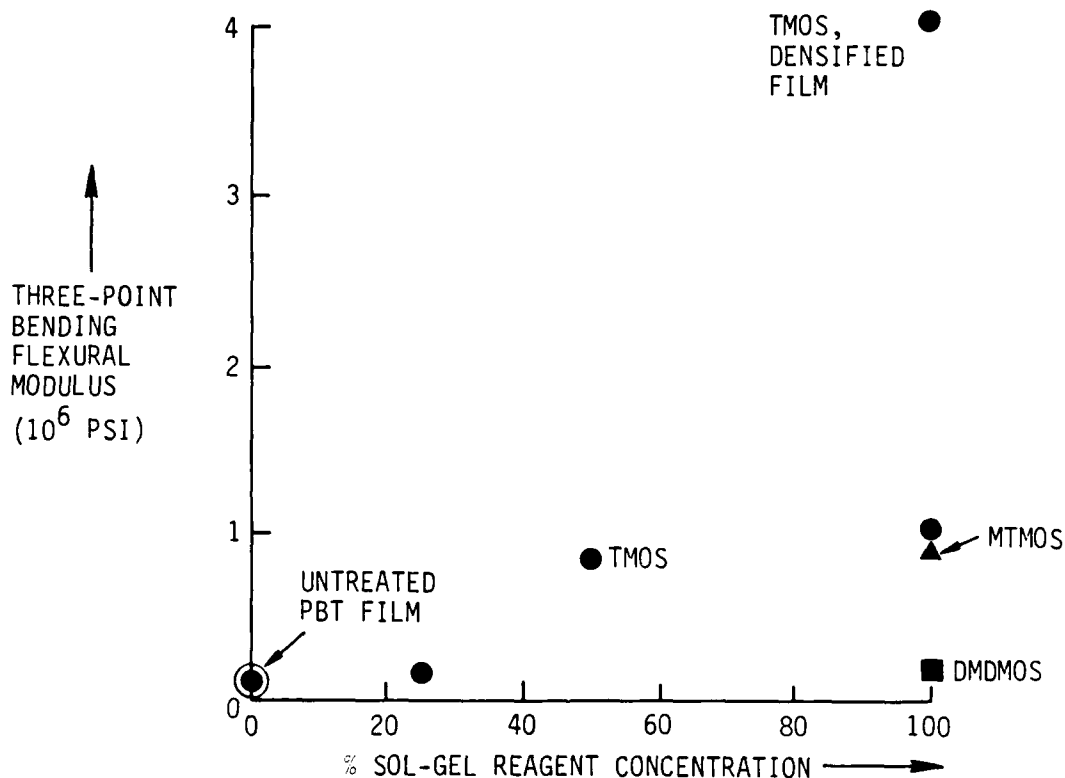


Figure 19. Variation of Three-Point Bending Modulus with Sol-Gel Reagent Concentration, Showing Improvement in Bending Modulus

Observations are as follows:

- The three-point bending test for single PBT films, although crude, allowed measurement of subtle differences in mechanical stiffness between PBT samples treated with various sol-gel reagents. Relationships between sol-gel treatment and observed bending modulus could therefore be ascertained.
- Increasing the concentration of sol-gel reagent during wet PBT film infiltration, increased the quantity of sol-gel glass introduced and increased the bending modulus (samples 2 to 5).

- Sol-gel infiltration of dimethylsiloxane elastomer into PBT film maintained original wet film thickness upon drying but did not increase bending modulus (sample 6).
- Increased heat-treatment of PBT films dramatically increased bending modulus (samples 2, 8, 9).

Figure 19 shows the dramatic increase in flexural modulus for PBT/sol-gel microcomposite film over untreated PBT film. This indicates that the sol-gel glass is reinforcing the PBT network. The TMOS densified film was hot pressed at 300°C and 1000 psi to further consolidate the microcomposite. The hot pressing increased the flexural modulus, and the sample fractured, revealing flexural strength. Other samples did not fracture before the 0.01 in. deflection was reached.

The calculated ultimate flexural strength was calculated at 96,000 psi, assuming the sample behaved as a beam in simple three-point bending. If we further assume the material is isotropic and behaves the same in tension and compression, then the ultimate compressive, tensile and flexural strength are identical, and equal to 96,000 psi. This is an overly simplified analysis, but the experimental work does show that the compressive strength and modulus can be significantly increased without seriously degrading the tensile properties.

5.4 Effect of Sol-Gel Infiltration upon PBT Film Specific Gravity

The specific gravity of PBT film is approximately 1.6, while that reported for silica glass is 2.2. Measurement of specific gravity of sol-gel-infiltrated PBT films should therefore provide an accurate measure of glass content for various test specimens. However, the presence of internal voids within microporous PBT films, introduces a potential source of error in measurement of specific gravity, tending to produce values lower than actual. Nevertheless, specific gravity values measured for PBT/sol-gel specimens correlated to silica contents comparable with those determined by chemical analysis of identical samples.

Infiltration of increasing amounts of sol-gel reagents into water-swollen PBT films increased the specific gravity by as much as 18 percent, as measured by flotation experiments. Carbon tetrachloride ($d = 1.58$)/methanol ($d = 0.8$) mixtures were adjusted until PBT film samples floated for at least 1 min. Specific gravity of the flotation medium was then determined by weighing an exact volume or the solution. The ratio of weights for flotation solution versus distilled water provided specific gravity of solution as well as suspended samples.

Table 8 illustrates changes in film specific gravity produced by infiltration of sol-gel glass precursor reagents.

The value of specific gravity obtained for stage-dried PBT film by flotation techniques was 1.34. The discrepancy between this value and the previously measured value of 1.6 for PBT film (11) can tend to lower the observed value for specific gravity.

Table 8. Effect of Sol-Gel Infiltration upon PBT Film Specific Gravity

Sample ID	Composition	Specific Gravity Increase (%)	Glass Content (Weight %)
SG-25-TMOS	Wet PBT film immersed in 25% TMOS	7	30
SG-50-TMOS	Wet PBT film immersed in 50% TMOS	15	36
SG-100-TMOS	Wet PBT film immersed in 100% TMOS	18	54
SG-100-DMDMOS	Wet PBT film immersed in 100% DMDMOS	2	23
SG-100-MTMOS	Wet PBT film immersed in 100% MTMOS	5	50
SG-100-Glycidyl	Wet PBT film immersed in 100% GPTMOS	7	13

Such voids are the result of film drying steps which were not conducted at sufficiently high temperatures and pressures to fully densify the PBT film. Additional film processing work will involve more sophisticated drying and heat treating steps to achieve dense films.

Figure 20 illustrates graphically the increase of specific gravity for PBT/glass films as glass content is increased. The calculated line shows the behavior for the specific gravity of SiO_2 equal to 1.375 times that of PBT. This is further evidence that glass content of PBT/glass microcomposites can be controlled by variation of reagent concentration during film infiltration.

5.5 Water Absorption of Sol-Gel Infiltrated PBT Films

To determine the effects of sol-gel infiltration upon PBT film water absorption, moisture content of PBT film samples was measured under two conditions: after vacuum-drying at 100°C , and after water immersion for 24 hr. Vacuum drying provided a measure of moisture adsorbed onto PBT film surfaces during storage at room temperature. The water immersion test measured the degree of hydrophilicity in films treated by various sol-gel reagents. Table 9 illustrates moisture content of sol-gel infiltrated PBT films following various treatments. The results indicated that increasing the silica content of PBT/glass microcomposites tended to increase the amount of water absorption. This can be explained by the fact that silica glass is hydrophilic, adsorbing significant quantities of moisture on the surface. Figure 21 graphically illustrates increases in water absorption of PBT/glass films with increasing sol-gel reagent concentration.

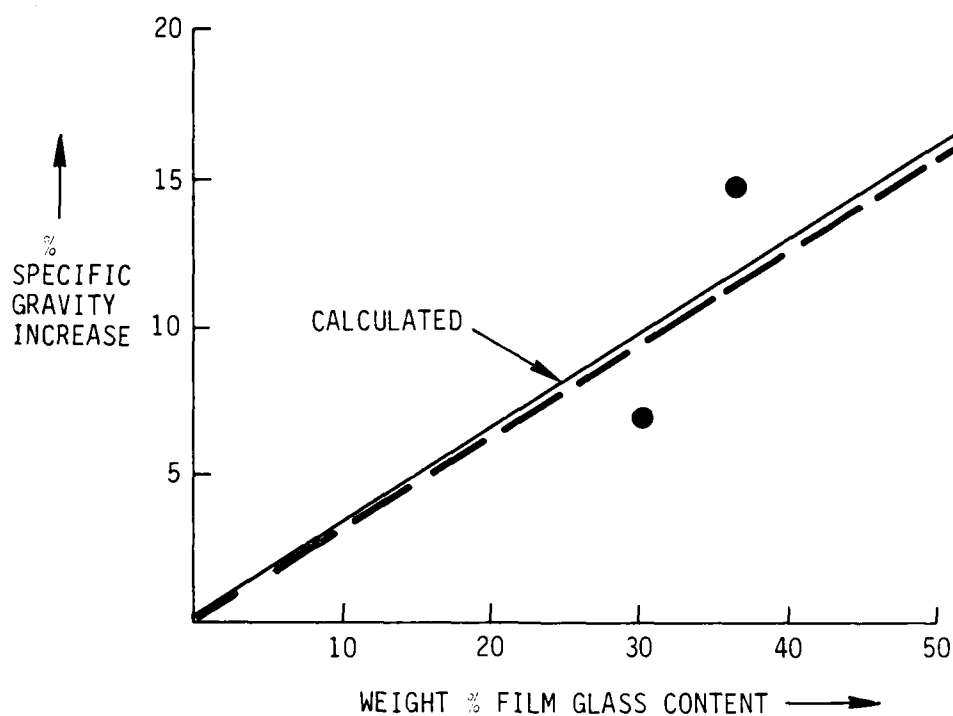


Figure 20. Variation of Specific Gravity Increase of PBT/Glass Microcomposite Films with Glass Content

Table 9. Water-Absorption of Sol-Gel-Infiltration PBT Films

Sample	Description	% Moisture Absorbed	
		Vacuum-Dried	Water-Immersed
PBT-stage-dried	Control. Dried at 250°C	0.6	3.3
PBT-heat-treated	Control. Dried at 250°C Heated at 400°C	1.1	2.9
SG-25-TMOS	Wet PBT film immersed in 25% TMOS. Dried at 250°C	2.4	4.8
SG-50-TMOS	Wet PBT film immersed in 50% TMOS. Dried at 250°C	1.7	6.4
SG-100-TMOS	Wet PBT film immersed in 100% TMOS. Dried at 250°C	6.6	11.8
SG-100-DMDMOS	Wet PBT film immersed in 100% DMDMOS. Dried at 250°C	2.4	5.2
SG-100-MTMOS	Wet PBT film immersed in 100% MTMOS. Dried at 250°C	1.8	4.6

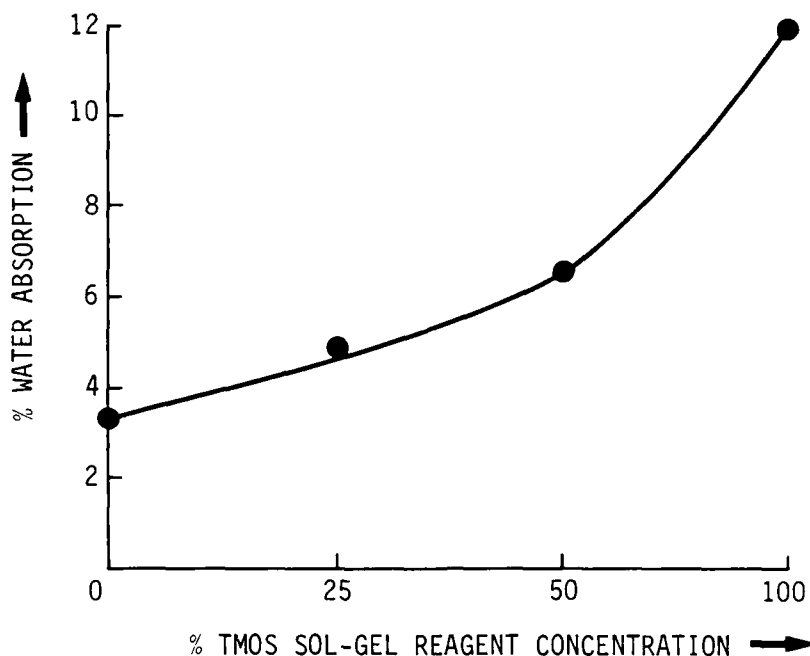


Figure 21. Variation of PBT/Glass Film Water Absorption with Increasing Sol-Gel Reagent Concentration

5.6 Thermogravimetric Analysis of Sol-Gel Infiltrated PBT Film

Thermogravimetric analysis of 100 percent TMOS-infiltrated PBT film that had been air-dried at room temperature indicated:

- Initial weight loss of 4.4 percent between room temperature and 150°C (H₂O, methanol)
- A very slight loss of ~0.5 percent between 300°C-500°C (CH₃OH from residual Si-OCH₃ groups)
- Rapid decomposition between 600°C-900°C, leaving a silica residue of 56 percent by weight.

By comparison, control PBT film lost 4 percent of its weight between 240°C-275°C and decomposed rapidly from 600°C to 700°C. The TGA traces are significant, because they indicate that the presence of significant quantities of sol-gel glass within the PBT film network did not affect the rate of thermal decomposition in air, as evidenced by similarity in TGA behavior. Figures 22 and 23 illustrate thermogravimetric behavior of sol-gel-infiltrated PBT film and control. The 56 percent silica residue for the PBT/TMOS sol-gel glass microcomposite compared favorably with a value of 54 percent silica obtained by chemical analysis techniques.

SAMPLE: RCPBTC REEL C CONTROL
SIZE: 7.95 MG
METHOD: FM 20DEG C/MIN 100CC N202
COMMENT: 20DEG C/MIN 100CC/MIN N202

TGA

FILE: M6003.02
OPERATOR: MICROTHERM
RUN DATE: 01/16/85 16:23

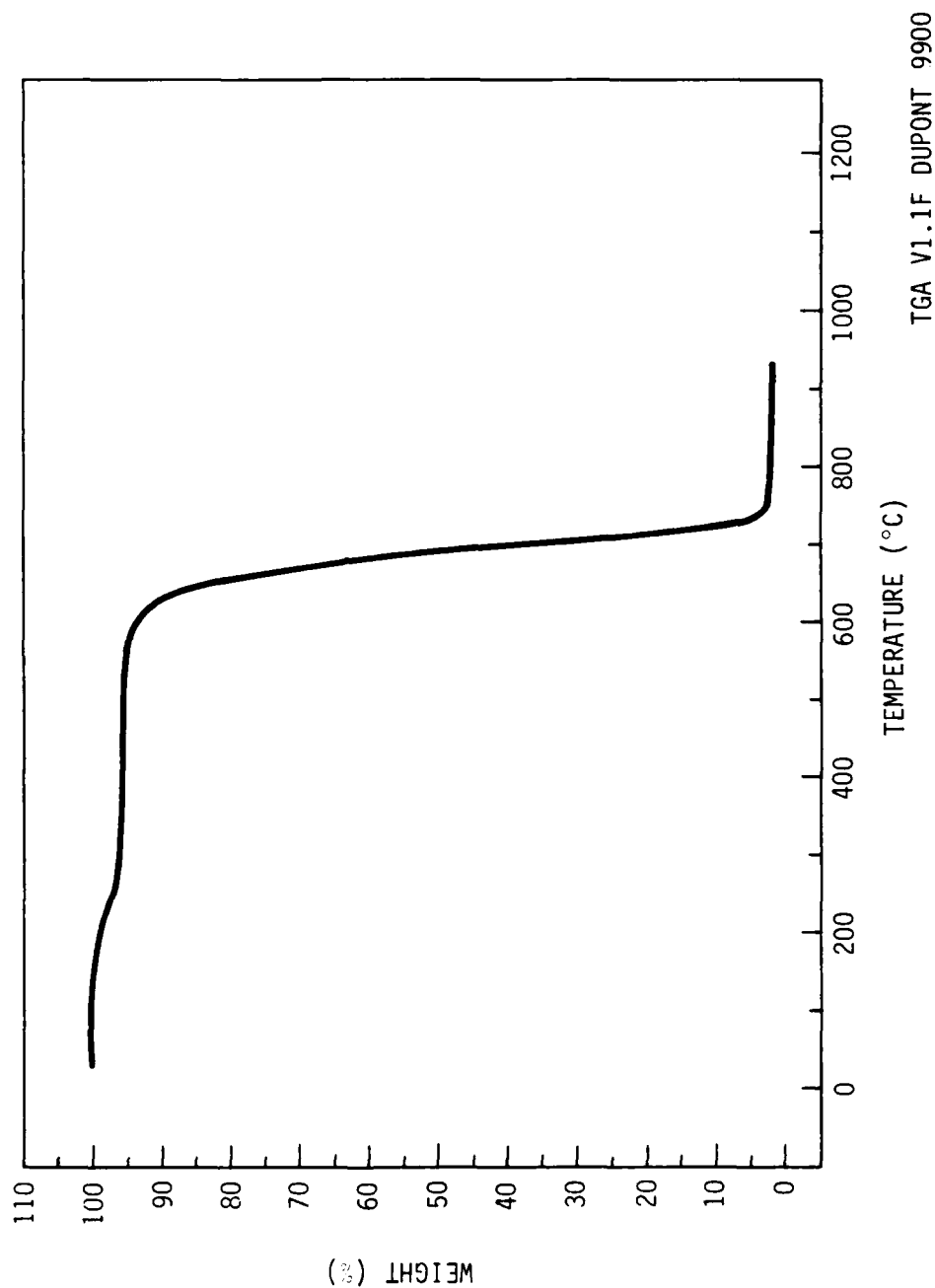


Figure 22. Thermogravimetric Analysis of PBT Control Film
Stage-Dried at 250°C

SAMPLE: R13SG100 1-9-85
 SIZE: 12.89 MG
 METHOD: FM 20DEG/MIN 100CC N202
 COMMENT: 20DEG/MIN 100CC/MIN N202 2
 TGA
 FILE: M6003.01
 OPERATOR: MICROTHERM
 RUN DATE: 01/16/85 15:22

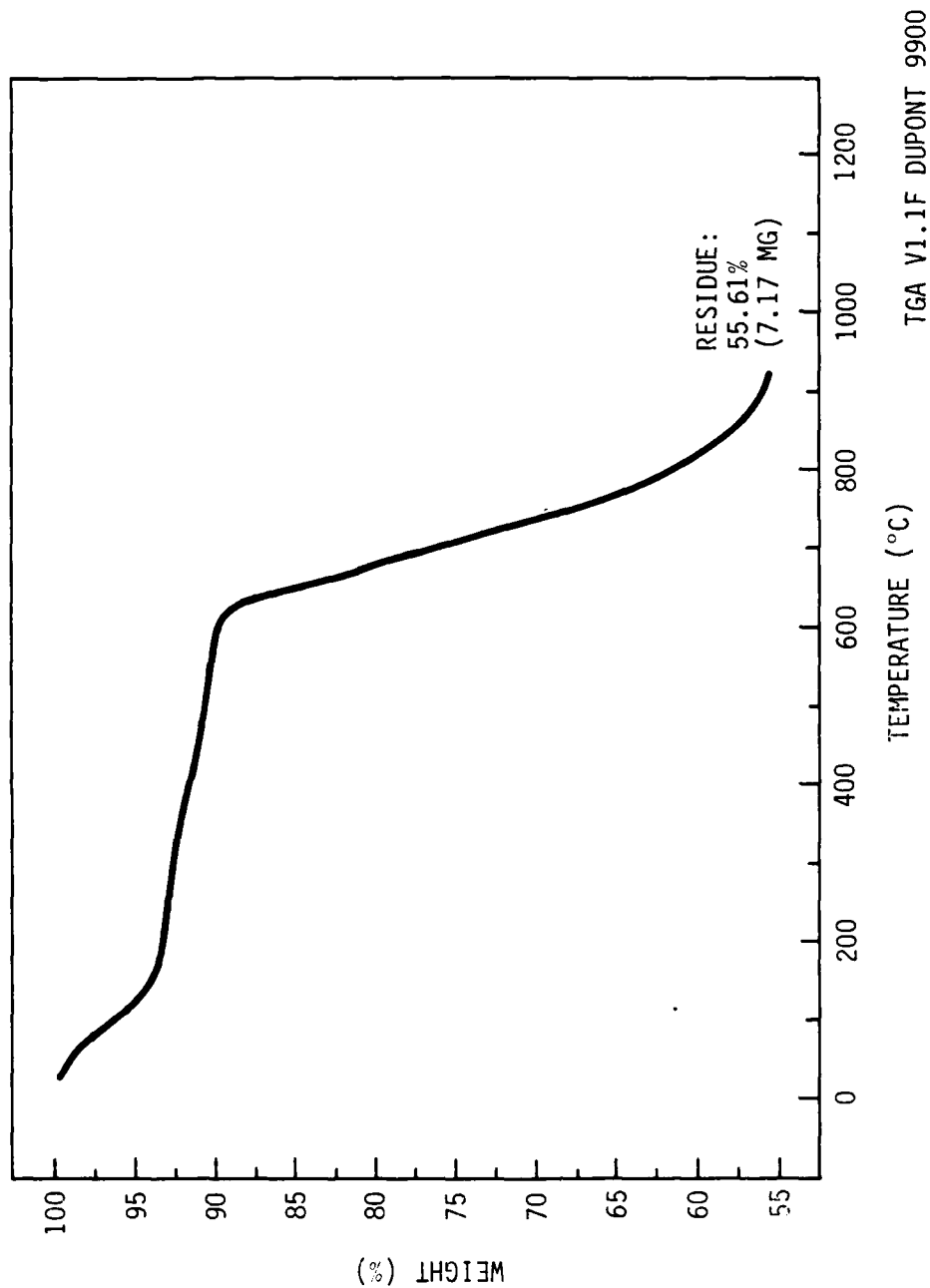


Figure 23. Thermogravimetric Analysis of PBT/TMOS sol-gel Microcomposite Film-Dried at Room Temperature

5.7 CTE for Sol-Gel PBT Films

The CTE of PBT/sol-gel glass film was measured with a Perkin-Elmer TMS-2 thermomechanical analyzer. The key component of the system is a quartz tube dilatometer which measures extension of a piece of film at cryogenic and elevated temperatures. A diagram of the quartz tube dilatometer is shown in Figure 24. The thermal expansion of the sample was measured over the temperature range -100° to 100°C using a tensile load of 10g.

Representative samples of PBT/sol-gel glass film and control film were cut into 1.0 mm x 10 mm specimens oriented along the machine direction (0 deg) and perpendicular to the machine direction (90 deg). The CTE results are listed in Table 10.

The addition of the SiO_2 glass into the PBT film produced the same change in CTE for both the 27 and 13 percent by weight silicon film. The 90 deg CTE increased by 10 ppm with the SiO_2 glass in addition to control PBT film. The 0 deg CTE appeared to decrease by 1 ppm, however this magnitude of change is the same order as the ± 1 ppm accuracy of the CTE analyzer.

Based on the results of Table 10, it is possible to increase the CTE of PBT films by adding glass. Furthermore with the proper starting PBT film and addition of the correct amount of glass, it should be possible to compensate for the negative CTE of PBT film with the positive CTE of glass, producing a near zero CTE film.

5.8 Photomicroscopy of PBT/Sol-Gel Glass Microcomposite Films

PBT/sol-gel glass films were examined by two photomicroscopic techniques namely, optical and scanning electron microscopy (SEM), in order to elucidate the internal structures of these unique materials. Optical microscopy provided bright, colored low-magnification pictures that revealed macrostructural details of film samples. Scanning electron microscopy offered higher magnification, enhanced contrast between areas differing in composition and the capability of analyzing selected, submicron sized target areas within the film for elemental composition. Results from the application of each technique to PBT/glass films are discussed in detail below.

Optical photomicrographs of densified, sol-gel glass-infiltrated PBT film interiors revealed smooth, yellow interiors that were vitreous in appearance. Careful film fracture provided smooth, yellow, glassy sheets of uniform appearance that contained IPNs of PBT microfibrils and sol-gel glass combined at the microcomposite level, beyond the resolution of optical microscopy. Thick PBT films also contained occasional, teardrop-shaped occlusions of glass, resulting from reaction of sol-gel reagent with water regions of similar shape formed within water-swollen PBT films during coagulation. In this way, sol-gel treatment provided useful information concerning the morphology of water-swollen PBT films.

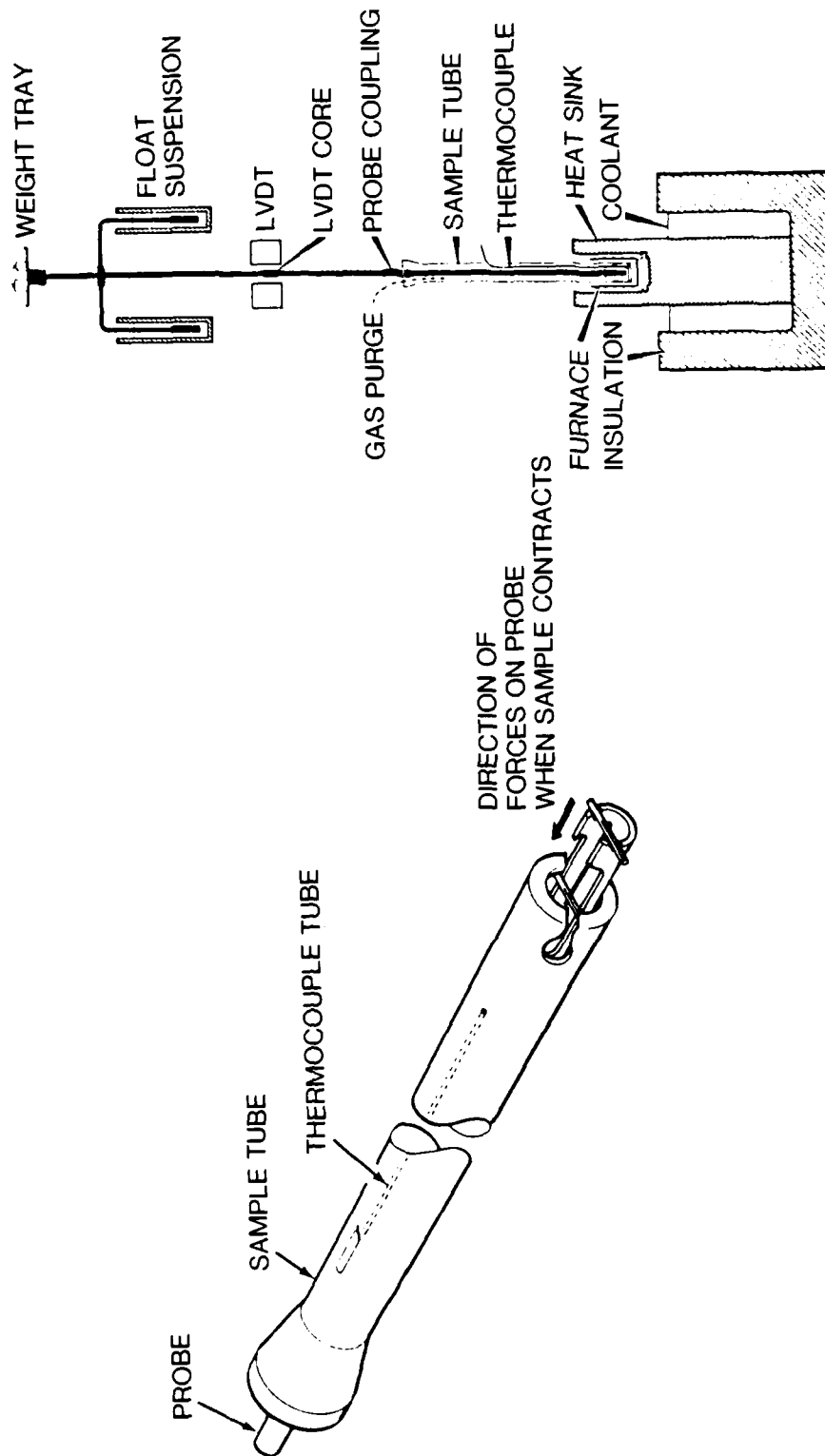


Figure 24. Quartz Tube Dilatometer

Table 10. CTE for Sol-Gel-Infiltrated PBT Films

Sample Conditions	Silicon Content (%)	CTE (ppm/°C)	
		α0 deg	α90 deg
A	27	-11	+5
Control A	<1	-10	-5
C	13	-10	+9
Control C	<1	-9	+0.3 - 0.7

SEM analysis of PBT/glass films confirmed the presence of sol-gel glass and PBT polymer within central regions of the film. Electron backscatter focusing was used to analyze interior sections of the film for the presence of silicon (glass) as well as sulfur (PBT).

Analysis of a submicron area within the interior of a PBT/glass microcomposite film indicated the presence of PBT and sol-gel glass, in approximately equal amounts by weight, as determined from the 2- to -1 silicon/sulfur ratio illustrated in Figures 25 and 26.

The effect of PBT/glass film densification at moderate temperatures and pressures (300°C/1000 psi) is illustrated in Figure 27, which shows sol-gel glass inclusions embedded within a matrix of PBT/sol-gel glass microcomposite. Evidently, film densification caused compression of PBT/glass regions, leaving glass incursions intact. Glass incursions were larger and more frequent in thick PBT/glass film samples which had probably contained water-swollen regions of low polymer orientation.

Examination of similar densified film samples prepared from thin, highly-stretched, wet films showed significantly fewer and smaller glass incursions.

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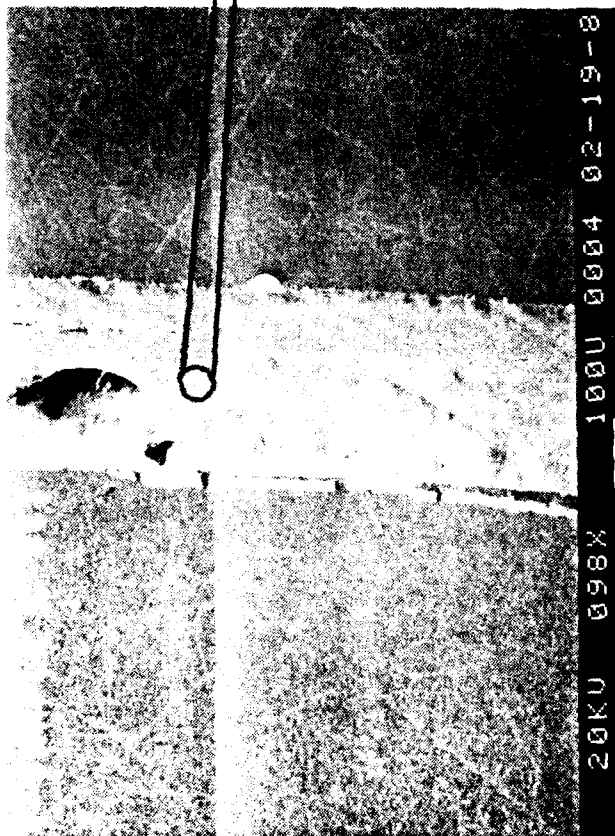


Figure 25. SEM of Epoxy Resin-Embedded PBT/Sol-Gel Silica IPN Microcomposite Film (50% SiO₂) Viewed on Edge (98X) before Densification (Sample C)
 Circle Shows Region of Film Analyzed for % Silicon (Glass) and % Sulfur (PBT)
 Using Backscattered Electron Imaging
 Figure Confirms the Presence of Glass and PBT

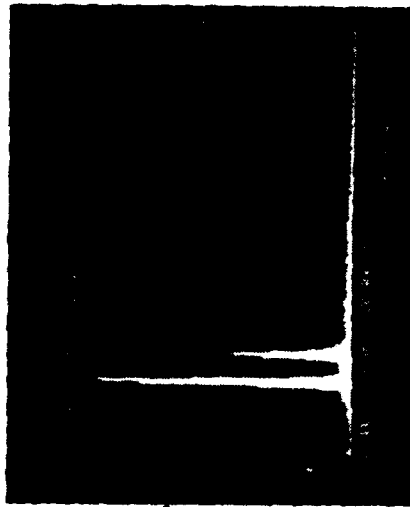


Figure 26. Backscattered Electron Analysis of Target Area (Film Matrix) in Figure 25, Confirming the Presence of Sol-Gel Glass (Silicon Peak on Left) and PBT Polymer (Sulfur Peak on Right) in an IPN

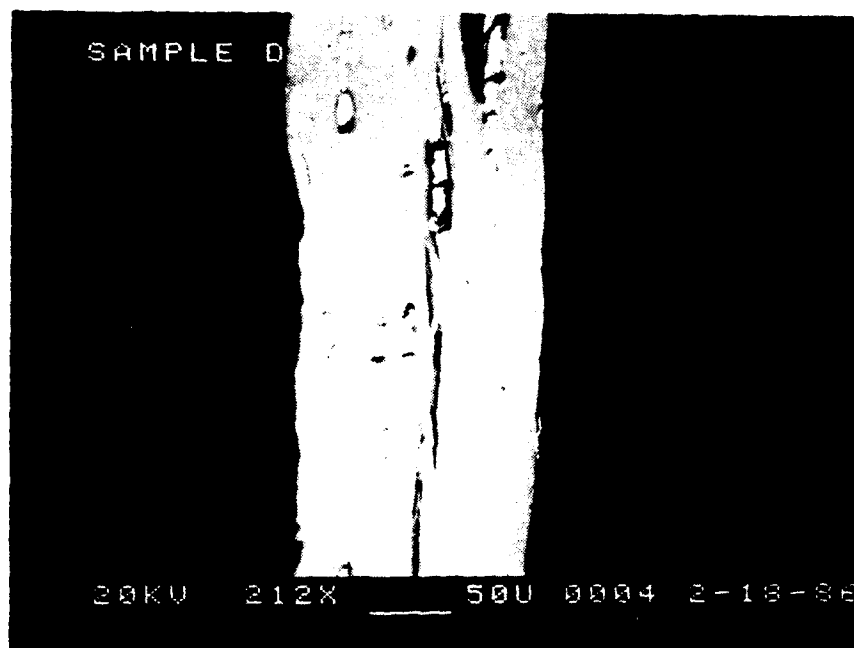


Figure 27. SEM of Epoxy Resin-Embedded, PBT Sol-Gel Glass Microcomposite Film (50% SiO₂) Viewed Edge-On, After Densification at 300°C/1000 psi. Inclusions of Sol-Gel Glass are Visible, Embedded within a PBT/Glass Microcomposite Network

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